

- **SOLID STATE**
- **LIQUID SOLUTION**
- **IONIC EQUILIBRIUM**

Copyright © reserved with Motion Edu. Pvt. Ltd. and Publications

All rights reserved. No part of this work herein should be reproduced or used either graphically, electronically, mechanically or by recording, photocopying, taping, web distributing or by storing in any form and retrieving without the prior written permission of the publisher. Anybody violating this is liable to be legally prosecuted.

Corporate Head Office

394 - Rajeev Gandhi Nagar Kota, (Raj.)
Ph. No. : 08003899588, 0744-2209671
IVRS No : 0744-2439051, 52, 53,
[www. motioniitjee.com](http://www.motioniitjee.com) , info@motioniitjee.com

THEORY AND EXERCISE BOOKLET

CONTENTS

S.NO.	TOPIC	PAGE NO.
SOLID STATE		
♦	THEORY WITH SOLVED EXAMPLES	5 – 35
♦	CLASS ROOM PROBLEMS	36 – 40
♦	EXERCISE - I (JEE Main)	41 – 49
♦	EXERCISE - II (JEE Advanced – Objective)	50 – 52
♦	EXERCISE - III (JEE Advanced)	53 – 62
♦	EXERCISE - IV (JEE Advanced – Previous Years).....	63 – 66
♦	ANSWER KEY	67 – 68
LIQUID SOLUTION		
♦	THEORY WITH SOLVED EXAMPLES	69 – 113
♦	EXERCISE - I (JEE Main)	114 – 124
♦	EXERCISE - II (JEE Advanced – Objective)	125 – 129
♦	EXERCISE - III (JEE Advanced)	130 – 145
♦	EXERCISE - IV (JEE Main & JEE Advanced – Previous Years).....	146 – 152
♦	ANSWER KEY	153 – 154
Ionic Equilibrium		
♦	THEORY WITH SOLVED EXAMPLES	155 – 195
♦	CLASS ROOM PROBLEMS	196 – 199
♦	EXERCISE - I (JEE Main)	200 – 209
♦	EXERCISE - II (JEE Advanced – Objective)	210 – 212
♦	EXERCISE - III (JEE Advanced)	213 – 231
♦	EXERCISE - IV (JEE Main & JEE Advanced – Previous Years).....	232 – 237
♦	ANSWER KEY	238 – 240

JEE SYLLABUS

• SOLID STATE

JEE - ADVANCED

Classification of solids, crystalline state, seven crystal systems (cell parameters a , b , c , α , β , γ), close packed structure of solids (cubic), packing in fcc, bcc and hcp lattices; Nearest neighbours, ionic radii, simple ionic compounds, point defects.

• LIQUID SOLUTION

JEE - ADVANCED

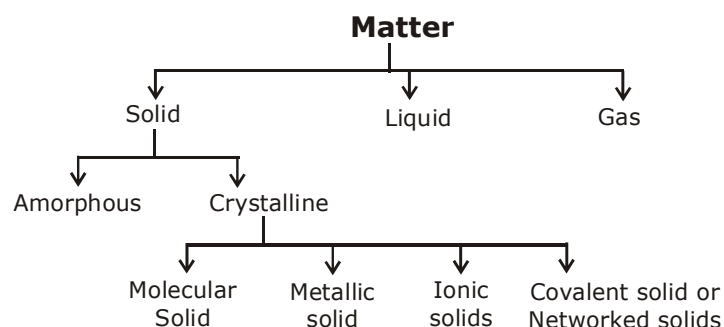
Raoult's law; Molecular weight determination from lowering of vapour pressure, elevation of boiling point and depression of freezing point.

• IONIC EQUILIBRIUM

JEE - ADVANCED

Solubility product, common ion effect, pH and buffer solutions; Acids and bases (Bronsted and Lewis concepts); Hydrolysis of salts.

Solid State



Solid	Liquid	Gas
(1) Have definite volume	Have definite volume	Have indefinite volume
(2) Their shape is fixed	Their shape is indefinite volume	Their shape is indefinite
(3) They have strongest intermolecular attraction. Hence their shape as well as volume is fixed	Their force of attraction is intermediate between solids and gases . So shape is variable but volume is fixed.	They have very weak force of attraction . Hence molecules are very - very loosely connected with each other and hence have neither shape nor volume fixed.

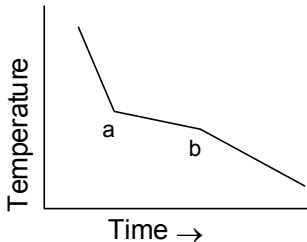
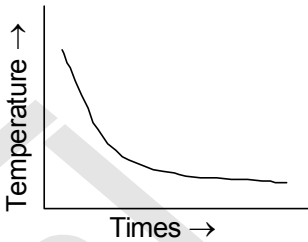
The outstanding macroscopic properties of gases are compressibility and fluidity.

In contrast, the most noticeable macroscopic features of crystalline solids are rigidity, incompressibility and characteristic geometry. We shall find that the explanation of these macroscopic properties in terms of the atomic theory involves the idea of lattice: a permanent ordered arrangement of atoms held together by forces of considerable magnitude.

Thus the extremes of molecular behaviour occur in gases and solids. In the former we have molecular chaos and vanishing intermolecular forces, and in the latter we have an ordered arrangement in which the interatomic forces are large.

Types of Solids

- Crystalline solids:** In a single crystal the regularity of arrangement of the pattern extends throughout the solid and all points are completely equivalent.
- Amorphous solids:** An amorphous solid differs from a crystalline substance in being without any shape of its own and has a completely random particle arrangements, i.e. no regular arrangement. Example: Glass, Plastic

Crystalline solid	Amorphous solid
1. The constituent particles are arranged in a regular fashion containing short range as well as long range order.	1. The constituent particles are not arranged in any regular fashion. There may be at the most some short range order only.
2. They have sharp melting point	2. They melt over a range of temperature.
3. They are anisotropic i.e., properties like electrical conductivity, thermal expansion, etc have different values in different direction.	3. They are isotropic i.e., properties like electrical conductivity, thermal expansion, etc have same value in different directions
4. They under go a clean cleavage.	4. They undergo an irregular cut
 <p>Temperature</p> <p>Time →</p> <p>Crystalline substances Cooling Curve.</p> <p>(figure 1a)</p>	 <p>Temperature ↑</p> <p>Times →</p> <p>Amorphous substances (cooling curve)</p> <p>(figure 1b)</p>

Classification of crystalline

Molecular solids : Those solids which consists of small molecules are called molecular solids.

(1) **Non - polar molecular solids :**

(electronegativity sequence ($F > O > N \approx Cl > Br > S > C \approx H$))

The solids which have zero dipole moment are called non-polar molecular solids.

The molecules are held together by weak Vander waal's forces . Hence they are either gas or liquids at room temperature.

They are poor conductor of electricity due to their non-polar nature.

(2) **Polar molecular solids :**

Those solids which have non-zero dipole moments are called polar molecular solids.

Polar molecular solids have dipole - dipole interaction, which is slightly stronger than vander waal's force and hence they have larger melting and boiling points than the non - polar molecular solids .

Example : Solid CO_2 , Solid NH_3

They are generally liquids or gases at room temperature.

(3) **Hydrogen bonded molecular solids :**

Those molecular solids which are bonded with each other by hydrogen bonds are called hydrogen bonded molecular solids .

Example : Ice

They are non-conductor of electricity

Generally they are liquid at room temperature or soft solids .

⇒ **IONIC SOLIDS :** All those solids whose constituent particles are ions are called ionic solids,

Example : NaCl, CsBr, AgBr, CsCl

⇒ **METALLIC SOLIDS :**

⇒ All those solids which are bonded by metallic bonds are called metallic solids.

⇒ Inner core electrons are immobile

⇒ Metallic solids show a great electrical conductivity due to availability of large number of free electrons whose movements constitute electric current.

Corporate Head Office : Motion Education Pvt. Ltd., 394 - Rajeev Gandhi Nagar, Kota-5 (Raj.)

- ⇒ Metallic solids are malleable and ductile.
- ⇒ Metallic solids have lustre.
- ⇒ Metallic solids have good thermal conductivity.

⇒ **COVALENT SOLIDS OR NETWORKED SOLIDS :**

Whenever electric field is applied, electrons move between the layers.

Graphite is a good conductor of electricity due to availability of free electrons.

Networked solids are hard and brittle.

Carbon - carbon bond has got partial double bond character in graphite.

Two layers in graphite are attached with each other by weak vander waal force.

Graphite can be used as a lubricant at high temperatures .

What is a crystal:

A crystalline solid consist of a large number of small units, called crystals, each of which possesses a definite geometric shape bounded by plane faces. The crystals of a given substance produced under a definite set of conditions are always of the same shape.

Unit Cells

In this topic we would be studying certain properties of a solid which depend only on the constituents of the solid and the pattern of arrangement of these constituents. To study these properties, it would be convenient to take up as small amount of the solid as possible because this would ensure that we deal with only the minimum number of atoms or ions. This smallest amount of the solid whose properties resemble the properties of the entire solid irrespective of the amount taken is called a **unit cell**. It is the smallest repeating unit of the solid. Any amount of the solid can be constructed by simply putting as many unit cells as required.

Bravais Lattices

Bravais (1848) showed from geometrical considerations that there are only seven shapes in which unit cells can exist. These are: (i) Cubic (ii) Orthorhombic (iii) Rhombohedral (iv) Hexagonal (v) Tetragonal (vi) Monoclinic and (vii) Triclinic. Moreover he also showed that there are basically four types of unit cells depending on the manner in which they are arranged in a given shape. These are : Primitive, Body Centered, Face Centered and End Centered. He also went on to postulate that out of the possible twenty eight unit cells (i.e. seven shapes \times four types in each shape = 28 possible unit cells), only fourteen actually would exist. These he postulated based only on symmetry considerations. These fourteen unit cells that actually exist are called **Bravais Lattices**.

Primitive Cubic Unit Cell

In a primitive cubic unit cell the same type of atoms are present at all the corners of the unit cell and are not present anywhere else. It can be seen that each atom at the corner of the unit cell is shared by eight unit cells (four on one layer, as shown, and four on top of these). Therefore, the volume occupied by a sphere in a unit cell is just one-eighth of its total volume. Since there are eight such spheres, the total volume occupied by the spheres is one full volume of a sphere. Therefore, a primitive cubic unit cell has effectively one atom. A primitive cubic unit cell is created in the manner as shown in the figure. Four atoms are present in such a way that the adjacent atoms touch each other. Therefore, if the length of the unit cell is 'a', then it is equal to $2r$, where r is the radius of the sphere. Four more spheres are placed on top of these such that they eclipse these spheres. The packing efficiency of a unit cell can be understood by calculating the **packing fraction**. It is defined as ratio of the volume occupied by the spheres in a unit cell to the volume of the unit cell and void fraction is

given as $1 - \text{Packing fraction}$. Therefore, $PF = \frac{\frac{4}{3}\pi r^3}{(2r)^3} \approx 0.52$. (This implies that 52 % of the volume of a unit cell is occupied by spheres). $\therefore VF \approx 0.48$

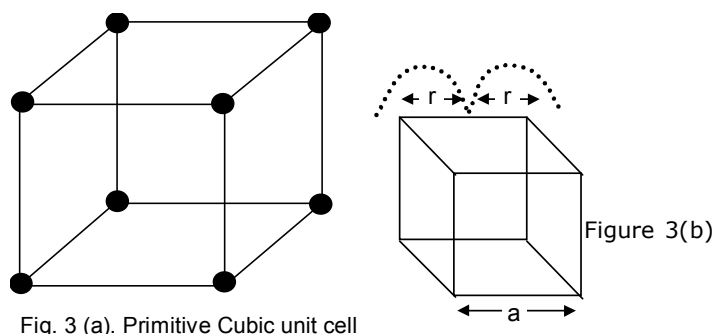


Fig. 3 (a). Primitive Cubic unit cell

Body Centered Cubic Unit Cell

A Body Centred unit cell is a unit cell in which the same atoms are present at all the corners and also at the center of the unit cell and are not present anywhere else. This unit cell is created by placing four atoms which are not touching each other. Then we place an atom on top of these four. Again, four spheres eclipsing the first layer are placed on top of this. The effective number of atoms in a Body Centered Cubic Unit Cell is 2 (One from all the corners and one at the center of the unit cell). Moreover, since in BCC the body centered atom touches the top four and the bottom four atoms, the

length of the body diagonal ($\sqrt{3}a$) is equal to $4r$. The packing fraction in this case is
$$= \frac{2 \times \frac{4}{3} \pi r^3}{\left(\frac{4r}{\sqrt{3}}\right)^3} \approx 0.68$$

$\therefore VF \approx 0.68$

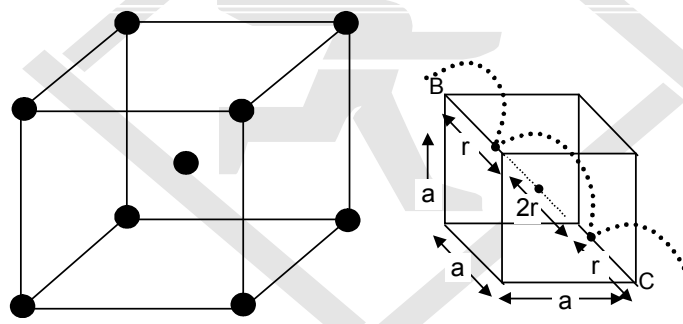


Fig. 4 (a) Body Centered Cubic unit cell

figure 4(b)

Face Centered Cubic Unit Cell

In a fcc unit cell, the same atoms are present at all the corners of the cube and are also present at the centre of each square face and are not present anywhere else. The effective number of atoms in fcc is 4 (one from all the corners, 3 from all the face centers since each face centered atom is shared by two cubes). Since, here each face centered atom touches the four corner atoms, the face diagonal of the cube ($\sqrt{2}a$) is equal to $4r$.

$$\therefore \text{packing fraction} = \frac{4 \times \frac{4}{3} \pi r^3}{\left(\frac{4r}{\sqrt{2}}\right)^3} \approx 0.74 \quad \therefore \text{VF} \approx 0.26$$

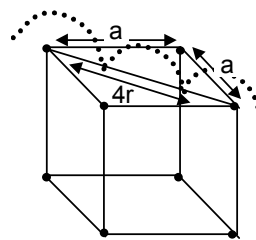


Figure 5(b)

Hexagonal Primitive Unit Cell

Each corner atom would be common to 6 other unit cells, therefore their contribution to one unit cell would be $1/6$. Therefore, the total number of atoms present per unit cell effectively is 6.

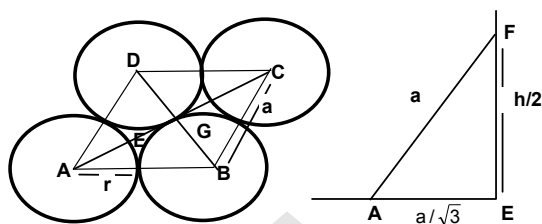


Figure 6(b) ABCD is the base of hexagonal unit cell $AD=AB=a$. The sphere in the next layer has its centre F vertically above E and it touches the three spheres whose centres are A, B and D.

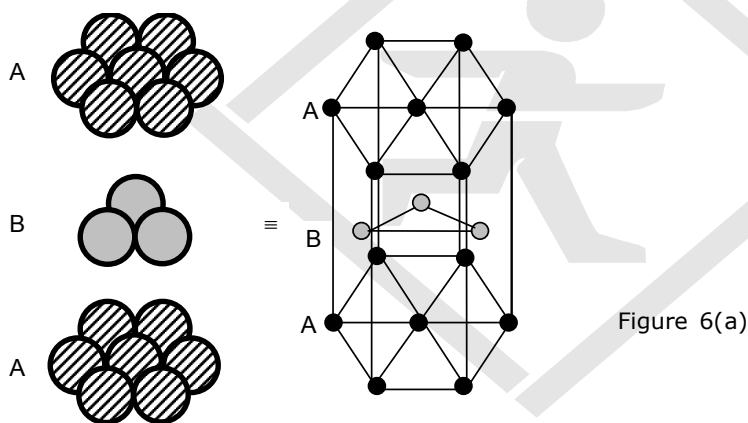


Figure 6(a)

HEXAGONAL CLOSE PACKING (HCP)

$$\therefore AE = \frac{2}{3} \times \frac{\sqrt{3}}{2} a = \frac{a}{\sqrt{3}} = \frac{2r}{\sqrt{3}}$$

$$\text{Hence } FE = \frac{h}{2} = \sqrt{(2r)^2 - \left(\frac{2r}{\sqrt{3}}\right)^2}$$

$$\therefore \text{The height of unit cell (h)} = 4r \sqrt{\frac{2}{3}}$$

The area of the base is equal to the area of six equilateral triangles, $= 6 \times \frac{\sqrt{3}}{4} (2r)^2$. The volume of the

$$\text{unit cell} = 6 \times \frac{\sqrt{3}}{4} (2r)^2 \times 4r \sqrt{\frac{2}{3}}.$$

Therefore

$$PF = \frac{6 \times \frac{4}{3} \pi r^3}{6 \times \frac{\sqrt{3}}{4} (2r)^2 \times 4r \sqrt{\frac{2}{3}}} = \mathbf{0.74} \quad \therefore \mathbf{VF \approx 0.26}$$

Density of crystal lattice

The density of crystal lattice is same as the density of the unit cell which is calculated as

$$\rho = \frac{\text{mass of unit cell}}{\text{volume of unit cell}} = \frac{\text{number of effective atoms} \times \text{mass number}}{\text{volume of unit cell} \times \text{Avogadro number}}$$

$$\rho = \frac{n \times M}{N_A \times V}$$

Seven crystal systems : The seven crystal systems are given below.

Crystal System	Bravais Lattices	Parameters of Unit Cell		Example
		Intercepts	Crystal angle	
1. Cubic	Primitive, Face Centered, Body Centered = 3	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Pb, Hg, Ag, Au Diamond, NaCl, ZnS
2. Orthorhombic	Primitive, Face Centered, Body Centered, End Centered = 4	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	KNO ₃ , K ₂ SO ₄
3. Tetragonal	Primitive, Body Centered = 2	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	TiO ₂ , SnO ₂
4. Monoclinic	Primitive, End Centered = 2	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$, $\beta \neq 90^\circ$	CaSO ₄ ·2H ₂ O
5. Triclinic	Primitive = 1	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	K ₂ Cr ₂ O ₇ , CaSO ₄ ·5H ₂ O
6. Hexagonal	Primitive = 1	$a = b \neq c$	$\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$	Mg, SiO ₂ , Zn, Cd
7. Rhombohedral	Primitive = 1	$a = b = c$	$\alpha = \gamma = 90^\circ$, $\beta \neq 90^\circ$	As, Sb, Bi, CaCO ₃
Total = 14				

Illustration 1: *Lithium borohydride crystallizes in an orthorhombic system with 4 molecules per unit cell. The unit cell dimensions are $a = 6.8\text{\AA}$, $b = 4.4\text{\AA}$ and $c = 7.2\text{\AA}$. If the molar mass is 21.76g. Calculate density of crystal.*

Solution: Since

$$\text{Density, } \rho = \frac{n \times \text{mol. wt}}{\text{Volume} \times \text{Av. No.}}$$

Here $n = 4$, Av. No. = 6.023×10^{23} , &

Volume = $V = a \times b \times c$

$$= 6.8 \times 10^{-8} \times 4.4 \times 10^{-8} \times 7.2 \times 10^{-8} \text{ cm}^3 = 2.154 \times 10^{-22} \text{ cm}^3$$

$$\therefore \text{density, } \rho = \frac{4 \times 21.76}{2.154 \times 10^{-22} \times 6.023 \times 10^{23}} = \mathbf{0.6708 \text{ gm/cm}^3}$$

Close Packing of Spheres

Atoms are space filling entities and structures can be described as resulting from the packing of spheres. The most efficient, called Closest Packing, can be achieved in two ways, one of which is called **Hexagonal Close Packing** (Hexagonal Primitive) and the other, Cubic Close Packing (ccp or fcc). Hexagonal close packing can be built up as follows:

Place a sphere on a flat surface. Surround it with six equal spheres as close as possible in the same plane. Looking down on the plane, the projection is as shown in Fig. 7 (a). Let us call this layer as the A layer. Now form over the first layer a second layer of equally bunched spheres, Fig 7 (b), so as to nestle into the voids. It will be clearly seen that once a sphere is placed over a void, it blocks the void which are adjacent to that void. Let us call this layer as the B layer. Now, it can be clearly seen that there are two types of voids created by the B layer of spheres. If a sphere is placed on the x - type of voids, it would resemble the A layer of spheres in the sense that it eclipses the spheres of the A layer. This arrangement (i.e., ABAB.....) is called the **hexagonal close packing (hcp) or hexagonal primitive**. On the other hand, if the spheres were to be placed on the y - type of voids, it would neither eclipse the A layer nor the B layer of spheres. This would clearly be a unique layer. Let us call this layer as the C layer (as seen in figure 7(c). This arrangement (i.e., ABCABC...) is called the **Cubic Close Packing (fcc)**.

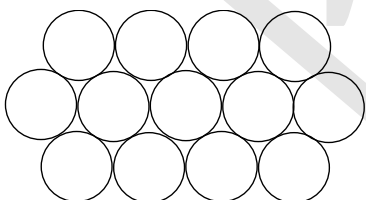


Fig. 7 (a) 'A' layer of spheres.

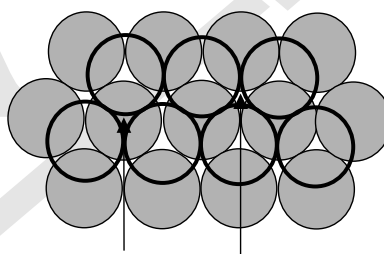


Fig. 7(b) 'A' and 'B' layer of spheres.

Exercise 1: It can be seen now that both fcc and Hexagonal Primitive Structure have the same packing fraction. Moreover this is also the highest packing fraction of all the possible unit cells with one type of atom with empty voids. Can you explain this?

Octahedral and Tetrahedral Voids

The close packing system involves two kinds of voids - tetrahedral voids and octahedral voids. The former has four spheres adjacent to it while the latter has six spheres adjacent to it. These voids are only found in either fcc or Hexagonal Primitive unit cells. Let us first consider a fcc unit cell (as shown in the figure 8(a)). Not all the atoms of the unit cell are shown (for convenience). Let us assume that there is an atom (different from the one that forms the fcc) at the center of an edge.

Let it be big enough to touch one of the corner atoms of the fcc. In that case, it can be easily

understood that it would also touch six other atoms (as shown) at the same distance. Such voids in an fcc unit cell in which if we place an atom it would be in contact with six spheres at equal distance (in the form of an octahedron) are called octahedral voids (as seen in fig. 8(a)).

On calculation, it can be found out that a fcc unit cell has four octahedral voids effectively. **The number of effective octahedral voids in a unit cell is equal to the effective number of atoms in that unit cell.**

Let us again consider a fcc unit cell. If we assume that one of its corners is an origin, we can locate a point having coordinates $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. If we place an atom (different from the ones that form the fcc) at this point and if it is big enough to touch the corner atom, then it would also touch three other atoms (as shown in the fig. 8(b)) which are at the face centers of all those faces which meet at that corner. Moreover, it would touch all these atoms at the corners of a regular tetrahedron. Such voids are called tetrahedral voids (as seen in fig. 8(b)).

Since there are eight corners, there are eight tetrahedral voids in a fcc unit cell. We can see the tetrahedral voids in another way. Let us assume that eight cubes of the same size make a bigger cube as shown in the fig. 8(c). Then the centers of these eight small cubes would behave as tetrahedral voids for the bigger cube (if it were face centered). **The number of tetrahedral voids is double the number of octahedral voids.** Therefore, the number of tetrahedral voids in hcp is 12.

Radius Ratio Rules

The structure of many ionic solids can be accounted for by considering the relative sizes of the positive and negative ions, and their relative numbers. Simple geometric calculations allow us to work out, as to how many ions of a given size can be in contact with a smaller ion. Thus, we can predict the coordination number from the relative sizes of the ions.

Co-ordination Number 3

The adjacent fig. 9(a) shows the smaller positive ion of radius r^+ is in contact with three larger negative ions of radii r^- . It can be seen that $AB = BC = AC = 2r^-$, $BD = r^- + r^+$. Further, the angle ABC is 60° , and the angle DBE is 30° . By trigonometry $\cos 30^\circ = (BE / BD)$. $BD = (BE / \cos 30^\circ)$, $r^+ + r^- = r^- / \cos 30^\circ = (r^- / 0.866) = r^- \times 1.155$, $r^+ = (1.155 r^-) - r^- = 0.155 r^-$, Hence $(r^+ / r^-) = 0.155$.

Co-ordination Number 4 (Tetrahedron)

Angle ABC is the tetrahedral angle of $109^\circ 28'$ and hence the angle ABD is half of this, that is $54^\circ 44'$.

In the triangle ABD, $\sin ABD = 0.8164 = AD / AB = \frac{r^-}{r^+ + r^-}$. Taking reciprocals, $\frac{r^+ + r^-}{r^-} = \frac{1}{0.8164} = 1.225$,

rearranging, we get, $\frac{r^+}{r^-} = 0.225$.

Co-ordination Number 6 (Octahedron) or 4 (Square Planar)

A cross section through an octahedral site is shown in the adjacent figure and the smaller positive ion (of radius r^+) touches six larger negative ions (of radius r^-). (Note that only four negative ions are shown in this section and one is above and one below the plane of the paper). It is obvious that $AB = r^+ + r^-$ and $BD = r^-$. The angle ABC is 45° in the triangle ABD. $\cos ABD = 0.7071 = (BD / AB) =$

$\frac{r^-}{r^+ + r^-}$. Rearranging, we get, $r^+ / r^- = 0.414$

Limiting radius ratio $\frac{r^+}{r^-} = x$	Co – ordination number	Shape	Example
$x < 0.155$	2	Linear	BeF_2
$0.155 \leq x < 0.225$	3	Planar Triangle	AlCl_3
$0.225 \leq x < 0.414$	4	Tetrahedron	ZnS
$0.414 \leq x < 0.732$	4	Square planar	PtCl_4^{2-}
$0.414 \leq x < 0.732$	6	Octahedron	NaCl
$0.732 \leq x < 0.999$	8	Body centered cubic	CsCl

Exercise 2:

The radius of a calcium ion is 94 pm and of an oxide ion is 146 pm. Predict the crystal structure of calcium oxide.

Classification of Ionic Structures

In the following structures, a black circle would denote a cation and a white circle would denote an anion. In any solid of the type A_xB_y , the ratio of the coordination number of A to that of B would be $y : x$.

Rock Salt Structure

Cl^- is forming a fcc unit cell in which Na^+ is in the octahedral voids. The coordination number of Na^+ is 6 and therefore that of Cl^- would also be 6. Moreover, there are 4 Na^+ ions and 4 Cl^- ions per unit cell. The formula is Na_4Cl_4 i.e., NaCl . The other substances having this kind of a structure are halides of all alkali metals except cesium halides and oxides of all alkaline earth metals except beryllium oxide.

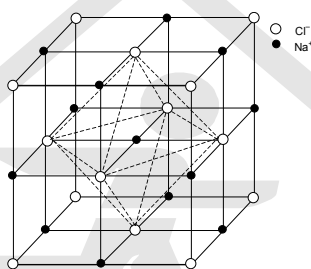


Figure 10 Unit cell structure of NaCl

Zinc Blende Structure

Sulphide ions are face centered and Zinc is present in alternate tetrahedral voids. Formula is Zn_4S_4 , i.e., ZnS . Coordination number of Zn is 4 and that of sulphide is also 4. Other substance that exists in this kind of a structure is BeO .

Fluorite Structures

Calcium ions are face centered and fluoride ions are present in all the tetrahedral voids. There are four calcium ions and eight fluoride ions per unit cell. Therefore the formula is Ca_4F_8 , (i.e., CaF_2). The coordination number of fluoride ions is four (tetrahedral voids) and thus the coordination number of calcium ions is eight. Other substances which exist in this kind of structure are UO_2 , and ThO_2 .

Anti-Fluorite Structure

Oxide ions are face centered and lithium ions are present in all the tetrahedral voids. There are four oxide ions and eight lithium ions per unit cell. As it can be seen, this unit cell is just the reverse of Fluorite structure, in the sense that, the positions of cations and anions is interchanged. Other substances which exist in this kind of a structure are Na_2O , K_2O and Rb_2O .

Cesium Halide Structure

Chloride ions are primitive cubic while the cesium ion occupies the center of the unit cell. There is one

chloride ion and one cesium ion per unit cell. Therefore the formula is CsCl. The coordination number of cesium is eight and that of chloride ions is also eight. Other substances which exist in this kind of a structure are all halides of cesium.

Corundum Structure

The general formula of compounds crystallizing in corundum structure is A_2O_3 . The closest packing is that of anions (oxide) in hexagonal primitive lattice and two-third of the octahedral voids are filled with trivalent cations. Examples are : Fe_2O_3 , Al_2O_3 and Cr_2O_3 .

Pervoskite Structure

The general formula is ABO_3 . One of the cation is bivalent and the other is tetravalent. Example: $CaTiO_3$, $BaTiO_3$. The bivalent ions are present in primitive cubic lattice with oxide ions on the centers of all the six square faces. The tetravalent cation is in the center of the unit cell occupying octahedral void.

Spinel and Inverse Spinel Structure

Spinel is a mineral ($MgAl_2O_4$). Generally they can be represented as $M^{2+}M_2^{3+}O_4$, where M^{2+} is present in one-eighth of tetrahedral voids in a FCC lattice of oxide ions and M^{3+} ions are present in half of the octahedral voids. M^{2+} is usually Mg, Fe, Co, Ni, Zn and Mn; M^{3+} is generally Al, Fe, Mn, Cr and Rh. Examples are $ZnAl_2O_4$, Fe_3O_4 , $FeCr_2O_4$ etc. Many substances of the type $M^{4+}M_2^{2+}O_4$ also have this structure. In an inverse spinel the ccp is of oxide ions, M^{2+} is in one-eighth of the tetrahedral voids while M^{3+} would be in one-eight of the tetrahedral voids and one-fourth of the octahedral voids.

Exercise 3: The unit cell of silver iodide (AgI) has 4 iodine atoms in it. How many silver atoms must be there in the unit cell.

Exercise 4: The co-ordination number of the barium ions, Ba^{2+} , in barium chloride (BaF_2) is 8. What must be the co-ordination number of the fluoride ions, F^- .

Imperfections in a Crystal

The discovery of imperfections in an other wise ideally perfect crystal is one of the most fascinating aspects of solid state science. An ideally perfect crystal is one which has the same unit cell and contains the same lattice points throughout the crystal. The term **imperfection** or **defect** is generally used to describe *any deviation of the ideally perfect crystal from the periodic arrangement of its constituents.*

Point Defect

If the deviation occurs because of missing atoms, displaced atoms or extra atoms, the imperfection is named as a **point defect**. Such defects can be the result of imperfect packing during the original crystallisation or they may arise from thermal vibrations of atoms at elevated temperatures because with increase in thermal energy there is increased probability of individual atoms jumping out of their positions of lowest energy. The most common point defects are the **Schottky defect** and the **Frenkel defect**. Comparatively less common point defects are the **metal excess defect** and the **metal deficiency defects**. All these defects have been discussed below in some details.

Schottky Defects: The defects arise if *some of the lattice points in a crystal are unoccupied*. The points which are unoccupied are called *lattice vacancies*. The existence of two vacancies, one due to a missing Na^+ ion and the other due to a missing Cl^- ion in a crystal of NaCl, is shown in figure 16. The crystal, as a whole remains neutral because the number of missing positive and negative ions is the same.

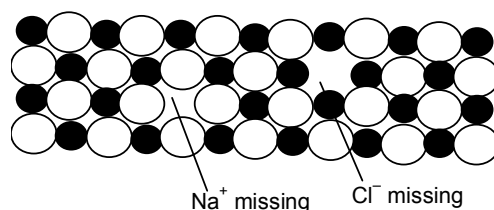


Figure 16

Schottky defects appear generally in ionic crystals in which *the positive and the negative ions do not differ much in size*. Sodium chloride and cesium chloride furnish good examples of ionic crystals in which Schottky defects occurs.

Frenkel Defects:

These defects arise when *an ion occupies an interstitial position between the lattice points*. This is shown in figure for the crystal of AgBr.

Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+
Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-
Ag^+	Br^-	Br^-	Ag^+	Ag^+	Br^-	Ag^+	Br^-	Ag^+
Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-

Figure 17: Frenkel Defects in a Crystal

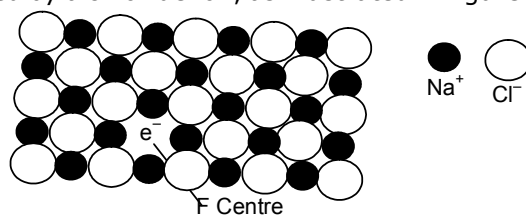
As can be seen, one of the Ag^+ ions occupies a position in the interstitial space rather than its own appropriate site in the lattice. A vacancy is thus created in the lattice as shown. It may be noted again that the crystal remains neutral since the number of positive ions is the same as the number of negative ions. The presence of Ag^+ ions in the interstitial space of AgBr crystal is responsible for the formation of a photographic image on exposure of AgBr crystals (i.e., photographic plate) to light.

ZnS is another crystal in which Frenkel defects appear. Zn^{2+} ions are entrapped in the interstitial space leaving vacancies in the lattice.

Frenkel defects appear in crystals in which the negative ions are much larger than the positive ions. Like Schottky defects, the Frenkel defects are also responsible for the conduction of electricity in crystals and also for the phenomenon of diffusion in solids.

Metal Excess Defects. The Colour Centres. It has been observed that if a crystal of NaCl is heated in sodium vapour, it acquires a yellow colour. This yellow colour is due to the formation of

a non-stoichiometric compound of sodium chloride in which there is a slight excess of sodium ions. What happens in this case is that some sodium metal gets doped into sodium chloride crystal which, due to the crystal energy, gets ionised into Na^+ and e^- . This electron occupies a site that would otherwise be filled by a chloride ion, as illustrated in figure.



F-centre in a Sodium chloride crystal

Figure 18

There is evidently an excess of metal ions although the crystal as a whole is neutral. A little reflection would show that there are six Na^+ sites adjacent to the vacant site occupied by the electron. The extra electron is thus shared between all the six Na^+ ions which implies that this electron is not localised at the vacant Cl^- site. On the other hand, this electron is similar to the delocalised π electrons present in molecules containing conjugate double bonds. Light is absorbed when this delocalised electron makes an easy transition from its ground state to an excited state. As a result, the non-stoichiometric form of sodium chloride **appears coloured**. Because of this, the sites occupied by the extra electrons are known as **colour centres**. These are also called **F-centres**. This name comes from the German word **Farbe** meaning **colour**. The non-stoichiometric sodium chloride may be represented by the formula $\text{Na}_{(1+\delta)}\text{Cl}$ where δ is the excess sodium metal doped in the crystal because of its exposure to sodium vapour.

Another common example of metal excess defects is the formation of a magenta coloured non-stoichiometric compound of potassium chloride by exposing the crystals of KCl to K metal vapour. The coloured compound contains an excess of K^+ ions, the vacant Cl^- sites being filled by electrons obtained by the ionization of the excess K metal doped in to the crystal.

Metal Deficiency Defects. In certain cases, one of the positive ions is missing from its lattice site and the extra negative charge is balanced by some nearby metal ion acquiring two charges instead of one. There is evidently, a deficiency of the metal ions although the crystal as a whole is neutral. This type of defect is generally found amongst the compounds of transition metals which can exhibit variable valency. Crystals of FeO, FeS and NiO show this type of defects. The existence of metal deficiency defects in the crystal of FeO is illustrated.


Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}
O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}
Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}		O^{2-}	Fe^{2+}	O^{2-}
O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{3+}	O^{2-}	Fe^{3+}	O^{2-}	Fe^{2+}
Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}

Figure 19

It is evident from the above discussion that all types of point defects result in the creation of vacancies or 'holes' in the lattice of the crystals. The presence of holes lowers the density as well as the lattice energy or the stability of the crystals. The presence of too many holes may cause a partial collapse of the lattice.

MAGNETIC PROPERTIES :

The macroscopic magnetic properties of material are consequence of magnetic moments associated with the individual electron. Each electron in an atom has magnetic moment due to two reasons. The first one is due to the orbital motion around the nucleus, and the second is due to the spin of electron around its own axis. A moving

electron may be considered to be a small current loop, generating a small magnetic field, and having a magnetic moment along its axis of rotation.

The other type of magnetic moment originates from electron spin which is directed along the spin axis. Each electron in an atom may be thought of as being a small magnet having permanent orbital and spin magnetic moments. The fundamental magnetic moment is Bohr Magneton, μ_B equal to $9.27 \times 10^{-24} \text{ Am}^2$. For each electron in an atom, the spin magnetic moment is $\pm \mu_B$ (depending upon the two possibilities of the spin). The contribution of the orbital magnetic moment is equal to $\mu_l \mu_B$, where μ_l is the magnetic quantum number of the electron.

Based on the behaviour in the external magnetic field, the substances are divided into different categories.

- (i) **Diamagnetic substances** : Substances which are weakly repelled by the external magnetic field are called diamagnetic substances, e.g. TiO_2 , NaCl , Benzene.
- (ii) **Paramagnetic substances** : Substances which are attracted by the external magnetic field are called paramagnetic substances, e.g., O_2 , Cu^{2+} , Fe^{3+} .
- (iii) **Ferromagnetic substances** : Substances which show permanent magnetism even in the absence of the magnetic field are called ferromagnetic substances e.g., Fe, Ni, Co, CrO_2 .
- (iv) **Ferrimagnetic Substances** : Substances which are expected to possess large magnetism on the basis of the unpaired electrons but actually have small net magnetic moment are called ferrimagnetic substances, e.g., Fe_3O_4 .
- (v) **Anti-ferromagnetic substances** : Substances which are expected to possess paramagnetic behaviour, ferromagnetism on the basis of unpaired electron but actually they possess zero net magnetic moment are called anti-ferromagnetic substances, e.g., MnO_2 .

Note : Ferromagnetic, Anti-ferromagnetic and Ferrimagnetic solids change into paramagnetic at some temperature. It may be further pointed out here that each ferromagnetic substance has a characteristic temperature above which no ferromagnetism is observed. This is known as **Curie Temperature**.

DIELECTRIC PROPERTIES :

Insulators do not conduct electricity because the electrons present in them are held tightly to the individual atoms or ions and are not free to move. However, when electric field is applied, polarization takes place because nuclei are attracted to one side and the electron cloud to the other side. Thus dipoles are formed. In addition to these dipoles, there may also be permanent dipoles in the crystal. These dipoles may align themselves in an ordered manner so that such crystals have a net dipole moment.

Such polar crystals show the following interesting properties :

- (i) **Piezoelectricity or Pressure - electricity** : When mechanical stress is applied on such crystals so as to deform them, electricity is produced due to displacement of ions. The electricity thus produced is called piezoelectricity and the crystals are called piezoelectric crystals. A few examples of piezoelectric crystals include Titanates of Barium and Lead, Lead zirconate (PbZrO_3), Ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) and Quarts. These crystals are used as pick-ups in record players where they produce electrical signals by application of pressure. They are also used in microphones, ultrasonic generators and sonar detectors.
- (ii) **Ferroelectricity** : In some of the piezoelectric crystals, the dipoles are permanently polarized even in the absence of the electric field. However, on applying, electric field, the direction of polarization changes, this phenomenon is called ferroelectricity due to analogy with ferromagnetism. Some examples of the ferroelectric solids are barium titanate (BaTiO_3), Sodium potassium tartarate (Rochelle salt) and Potassium dihydrogen phosphate (KH_2PO_4).

Note : All ferroelectric solids are piezoelectric but the reverse is not true.

- (iii) **Anti-ferroelectricity** : In some crystals, the dipoles align themselves in such a way that alternately, they point up and down so that the crystal does not possess any net dipole moment. Such crystals are said to be anti-ferroelectric. A typical example of such crystals is Lead zirconate (PbZrO_3).

Superconductivity :

A substance is said to be superconducting when it offers no resistance to the flow of electricity.

Isomorphism :

The property shown by crystals of different chemical substances which exhibit the same crystalline form is known as isomorphism.

Such substances have similar chemical formula, e.g., $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ and $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$

- Chemically substances having same type of formulae are not necessarily Isomorphous.

MAGNETIC PROPERTIES OF CRYSTALS

Properties	Information	Magnetic Alignment	Example	Application
1. Diamagnetic	Repelled weakly in magnetic field. Such solids have only paired electrons.	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	Benzene NaCl, TiO_2 , V_2O_5 , etc.	Insulators
2. Paramagnetic	Have unpaired electrons; weakly attracted in magnetic field. They cannot be permanently magnetised.	$\nearrow \searrow \rightarrow \uparrow \searrow \nearrow$	O_2 , VO, CuO, TiO	Electronic devices
3. Ferromagnetic	Also, have unpaired electrons. Strongly attracted in magnetic field. Such solids can be permanently magnetised. On heating to a temperature called Curie Point, these solids change to paramagnetic solid.	$\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow$	Fe, Ni, Co, CrO_2	CrO_2 is used in audio, video tapes.
4. Antiferromagnetic	In these solids change electrons align themselves in such a way that resultant magnetic moment is zero.	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	Cr_2O_3 , CoO, Co_3O_4 , Fe_2O_3 , MnO, MnO_2	Used in the instruments of magnetic susceptibility measurement
5. Ferrimagnetic	unpaired electrons align themselves in such way that there is a net magnetic moment.	$\uparrow\downarrow \uparrow \downarrow\downarrow \downarrow\downarrow$ OR $\uparrow\uparrow \downarrow\downarrow \downarrow\downarrow \uparrow\uparrow$ and so on	Fe_3O_4 , ferrites	—

ELECTRICAL PROPERTIES OF CRYSTALS

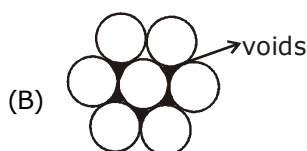
Properties	Information	Dipolar Property	Example	Application
1. Piezoelectricity	When a crystal of dielectrics is subjected to mechanical stress, then small magnitude current is produced. It is called direct Piezoelectric effect.	Development of charge in some part of crystal	Quartz and Rochelle salt	
2. Anti piezoelectricity	In some solids, electric field develops mechanical effect.	Crystal suffers elastic deformation in an electric field	—	
3. Ferroelectricity	Piezoelectric crystals having permanent dipoles are said to possess ferroelectricity	$\uparrow\uparrow\uparrow\uparrow\uparrow$	BaTiO_3 , KH_2PO_4 Rochelle salt	Electromagnetic appliances.
4. Anti ferroelectricity	Piezoelectric crystals with zero dipole are said to possess anti ferroelectricity.	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	PbZrO_3 Lead zirconate	
5. Pyroelectricity	Some polar crystals produce electric impulse on heating.	—	Crystals of tartaric acid.	Used in fire alarms, thermostat.

Solved Objective Problems

Ex.1 Select write statement (s)

- (A) 8 Cs^+ ions occupy the second nearest neighbour locations of a Cs^+ ion
 (B) Each sphere is surrounded by six voids in two dimensional hexagonal close packed layer
 (C) If the radius of cations and anions are 0.3 \AA and 0.4 \AA then coordinate number of cation of the crystal is 6.
 (D) In AgCl , the silver ion is displaced from its lattice position to an interstitial position such a defect is called a frenkel defect.

Sol. (A) 6 Cs^+ ion second nearest neighbour



(C) $\frac{r_+}{r_-} = 0.75$ (BCC) 8 : coordination no.

(D) True

Ex.2 Which of the following statement is/are incorrect in the rock-salt structure if an ionic compounds ?

- (A) coordination number of cation is four where as that of anion is six.
 (B) coordination number of cation is six where as that of anion is four.
 (C) coordination number of each cation and anion is four.
 (D) coordination number of each cation and anion is six.

Sol. Coordination no. of cation = 6
 coordination no of anion = 6

Ex.3 Which of the following statements are correct :

- (A) The coordination number of each type of ion in CsCl is 8.
 (B) A metal that crystallises in BCC structure has a coordination number 12.
 (C) A unit cell of an ionic crystal shares some of its ions with other unit cells
 (D) The length of the unit cell in NaCl is 552 pm . [$r_{\text{Na}^+} = 95 \text{ pm}$; $r_{\text{Cl}^-} = 181 \text{ pm}$]

Sol. $r_+ + r_- = a/2$
 $(95 + 181) = a/2$
 $\Rightarrow a = 276 \times 2$
 $a = 552 \text{ pm}$

Ex.4 A cubic solid is made up of two elements A and B. Atoms B are at the corners of the cube and A at the body centre. What is the formula of compound.

Sol. A = 1 (Body center)

$$B = 8 \times \frac{1}{8} = 1 \text{ (for corner)}$$

formula = AB

Ex.5 A compound alloy of gold and copper crystallizes in a cubic lattice in which gold occupy that lattice point at corners of the cube and copper atom occupy the centres of each of the cube faces. What is the formula of this compound.

Sol. $\text{Au} = \frac{1}{8} \times 8 = 1$, $\text{Cu} = \frac{1}{2} \times 6 = 3$

Formula = AuCu

Ex.6 A cubic solid is made by atoms A forming close pack arrangement, B occupying one. Fourth of tetrahedral void and C occupying half of the octahedral voids. What is the formula of compound.

Sol. $A = \frac{1}{2} \times 6 + \frac{1}{8} \times 8 = 4$

$$B = \frac{8}{4} \text{ no. of void (tetrahedral)}$$

$$= 2$$

$$C = \text{Total no. of octahedral voids} / 2$$

$$\text{no. of octahedral voids (effective)}$$

$$= 1 + 12 \times 1/4 = 4$$

$$\text{Bodycenter edgecentre}$$

$$C = 4/2 = 2$$

$$\text{formula} = A_4B_2C_2$$

Ex.7 What is the percent by mass of titanium in rutile, a mineral that contain Titanium and oxygen, if structure can be described as a closet packed array of oxide ions, with titanium in one half of the octahedral holes. What is the oxidation number of titanium ?

Sol. $O^{2-} = \frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 4$

$$Ti = \frac{(1 + 12 \times 1/4)}{2} = \frac{4}{2} = 2$$

$$TiO_2 \text{ formula}$$

$$Ti \text{ (At mass)} = 47.88$$

$$\% Ti = \frac{47.88}{79.88} \times 100 = 59.94 \%$$

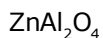
$$\text{Ox. State} = +4$$

Ex.8 Spinel is a important class of oxides consisting of two types of metal ions with the oxide ions arranged in CCP pattern. The normal spinel has one-eighth of the tetrahedral holes occupied by one type of metal ion and one half of the octahedral hole occupied by another type of metal ion. Such a spinel is formed by Zn^{2+} , Al^{3+} and O^{2-} , with Zn^{2+} in the tetrahedral holes. Give the formulae of spinel.

Sol. $Zn^{2+} = 8/8 = 1$

$$Al^{3+} = 4/2 = 2$$

$$O^{2-} = \text{CCP (4)}$$



$$Zn^{2+} = \frac{1}{8} \times 8 \quad \text{octahedral voids}$$

$$Al^{2+} = \frac{1}{2} \times 4 \quad \text{octahedral voids}$$

$$O^{2-} = \text{CCP} \quad \text{arrangement (1+3) = 4}$$

Ex.9 Iron occurs as bcc as well as fcc unit cell. If the effective radius of an atom of iron is 124 pm. Compute the density of iron in both these structures.

Sol. In bcc $z=2$

$$\rho = \frac{2 \times 56}{N_A(a^3)}, \quad r = \frac{a\sqrt{3}}{4} \Rightarrow a = \frac{4 \times 124}{\sqrt{3}} \text{ in pm}$$

$$\rho = \frac{2 \times 56}{\left(\frac{4 \times 124}{\sqrt{3}}\right)^3 \times 10^{-36} \times 6.022 \times 10^{23}} = 7.92 \times 10^6 \text{ g/cm}^3$$

In FCC, $Z = 4$, $\rho = \frac{4 \times 56}{\left(\frac{4 \times 124}{\sqrt{2}}\right)^3 \times 10^{-36} \times 6.022 \times 10^{23}} = 8.6 \text{ g/cm}^3$

Ex.10 A closed packed structure of uniform spheres has the edge length of 534 pm. Calculate the radius of sphere, if it exist in

(A) simple cubic lattice

(B) BCC lattice

(C) FCC lattice

Sol. (A) Simple cubic lattice

$$2r = a \Rightarrow r = \frac{a}{2} = \frac{534}{2} = 267 \text{ pm}$$

$$(B) 4r = a\sqrt{3} \Rightarrow r = \frac{534\sqrt{3}}{4} = 231.23 \text{ pm}$$

$$(C) 4r = a\sqrt{2} \Rightarrow r = \frac{534\sqrt{2}}{4} = 188.79 \text{ pm}$$

Ex.11 Calculate the density of diamond from the fact that it has face centered cubic structure with two atoms per lattice point and unit cell edge length of 3.569 Å.

Sol. In simple FCC $Z = 4$

but here from question two atoms per lattice point

$$\Rightarrow z = 8 \Rightarrow \rho = \frac{8 \times M / N_A}{a^3} = \frac{\left(\frac{8 \times 12}{6.022 \times 10^{23}}\right)}{(3.569 \times 10^{-10})^3} \text{ g/m}^3 = 3.5 \times 10^6 \text{ g/m}^3 = 3.5 \text{ g/cm}^3$$

Ex.12 An element crystallizes into a structure which may be described by a cubic type of unit cell having one atom on each corner of the cube and two atoms on one of its body diagonals. If the volume of this unit cell is $24 \times 10^{-24} \text{ cm}^3$ and density of element is 7.2 g cm^{-3} , calculate the number of atoms present in 200 g of element.

Sol. $z = 3$

$$7.2 = \frac{3 \times \frac{M}{N_A}}{24 \times 10^{-24}} \Rightarrow M = 34.68$$

$$\text{no. of atoms in 200 gram} = \frac{200}{34.68} \times 6.022 \times 10^{23} = 3.47 \times 10^{24} \text{ atoms}$$

Ex.13 Silver has an atomic radius of 144 pm and the density of silver is 10.6 g cm^{-3} . To which type of cubic crystal, silver belongs?

Sol. $10.6 \times 10^6 \text{ g/m}^3 = \frac{z \times 108 / N_A}{a^3} \Rightarrow \frac{a^3}{z} = 1.692 \times 10^{-29}$

$$\text{PF} = \frac{z \times \frac{4}{3} \pi r^3}{a^3} \times 100 = \frac{4/3 \pi (144 \times 10^{-12})^3}{1.69 \times 10^{-29}} \times 100 \approx 74 \% \Rightarrow \text{F.C.C.}$$

Ex.14 *AgCl has the same structure as that of NaCl. The edge length of unit cell of AgCl is found to be 555 pm and the density of AgCl is 5.561 g cm^{-3} . Find the percentage of sites that are unoccupied.*

Sol.
$$\rho = \frac{\left(4 \times \frac{143.5}{6.022 \times 10^{23}}\right)}{(555 \times 10^{-12})^3} = 5.575 \text{ g / cm}^3$$

If 100% sites occupied $\rho = 5.575$ but density is 5.561

$$\% \text{ sites occupied} = \frac{5.561}{5.575} \times 100$$

$$\% \text{ sites unoccupied} = 100 - (99.75) \% = 0.25\%$$

Ex.15 *Xenon crystallises in the face-centred cubic lattice and the edge of the unit cell is 620 pm. What is the nearest neighbour distance and what is the radius of xenon atom ?*

Sol. nearest neighbour distance = $2r$ (in FCC)

$$\Rightarrow a\sqrt{2} = 4r$$

$$\Rightarrow 2r = \frac{a}{\sqrt{2}} = \frac{620}{1.414}$$

$$2r = 438.47$$

$$r = 219.23$$

Ex.16 *The two ions A^+ and B^- have radii 88 and 200 pm respectively. In the closed packed crystal of compound AB, predict the co-ordination number of A^+ .*

Sol. $\frac{r_+}{r_-} = 0.44$

It could be square planar

or

octahedral void

but for closed packed crystal

\Rightarrow it is octahedral void

= coordination no. = 6

Ex.17 *CsCl has the bcc arrangement and its unit cell edge length is 400 pm. Calculate the interionic distance in CsCl.*

Sol. interionic distance

$$r_+ + r_- = \frac{a\sqrt{3}}{2} = 200\sqrt{3} = 346.4$$

Ex.18 *Gold crystallizes in a face centered cubic lattice. If the length of the edge of the unit cell is 407 pm, calculate the density of gold as well as its atomic radius assuming it to be spherical. Atomic mass of gold = 197 amu.*

Sol. FCC : $Z = 4$

$$\rho = \frac{\left(4 \times \frac{197}{6.022 \times 10^{23}}\right)}{(407 \times 10^{-12})^3} \text{ g / m}^3 = 19.41 \times 10^6 \text{ g / m}^3 = 19.41 \text{ g / cm}^3$$

$$\& 2r = \frac{a\sqrt{2}}{2} \Rightarrow r = \frac{a\sqrt{2}}{4} = 143.9 \text{ pm}$$

Ex.19 The density of KBr is 2.75 g cm^{-3} . The length of the edge of the unit cell is 654 pm. Show that KBr has face centered cubic structure.

($N = 6.023 \times 10^{23} \text{ mol}^{-1}$, At. mass : K = 39, Br = 80)

Sol.
$$\rho = \frac{z \times \frac{M}{N_A}}{a^3}$$

$$\frac{a^3}{z} = \frac{119 / 6.023 \times 10^{23}}{2.75}$$

$$= 7.18 \times 10^{-23}$$

$$z = (654 \times 10^{-10})^3 / (7.18 \times 10^{-23}) \approx 4$$

\Rightarrow FCC

Ex.20 An element crystallizes in a structure having FCC unit cell of an edge 200 pm. Calculate the density, if 200 g of this element contains 24×10^{23} atoms.

Sol. 24×10^{23} atom contain by 200g

6×10^{23} atom contains by

$$\frac{200}{4} \text{ g} = 50 \text{ g}$$

$M \approx 50 \text{ g/mole}$

$$\rho = \frac{4 \times \frac{50}{6 \times 10^{23}}}{(200 \times 10^{-10})^3} = \frac{4 \times 50}{6 \times 10^{23} \times 8 \times 10^{-24}}$$

$$= \frac{4 \times 50}{48 \times 10^{-1}} = \frac{2000}{48}$$

$$\rho = 41.67 \text{ g/cm}^3$$

Ex.21 The effective radius of the iron atom is 1.42 \AA . If has FCC structure. Calculate its density (Fe = 56 amu)

Sol.
$$\rho = \frac{4 \times \frac{56}{N_A}}{a^3}$$

$$\sqrt{2}a = 4r \Rightarrow a = \frac{4r}{\sqrt{2}}$$

$$= 4.016 \text{ \AA}$$

$$\rho = \frac{4 \times 56}{6.022 \times 10^{23} \times (4.016)^3 \times 10^{-30}}$$

$$= 0.574 \times 10^7 \text{ g/m}^3$$

$$= 5.74 \times 10^6 \text{ g/m}^3$$

$$\rho = 5.74 \text{ g/cm}^3$$

Ex.22 A crystal of lead (II) sulphide has NaCl structure. In this crystal the shortest distance between Pb^{+2} ion and S^{2-} ion is 297 pm. What is the length of the edge of the unit cell in lead sulphide? Also calculate the unit cell volume.

Sol. NaCl type FCC

$$r_+ + r_- = \frac{a}{2} = 297$$

$$\Rightarrow a = 297 \times 2 = 594 \text{ pm}$$

$$= 594 \times 10^{-10} \text{ cm}$$

$$= 5.94 \times 10^{-8} \text{ cm}$$

$$a^3 = \text{volume} = 2.096 \times 10^{-22} \text{ cm}^3$$

Ex.23 If the length of the body diagonal for CsCl which crystallises into a cubic structure with Cl^- ions at the corners and Cs^+ ions at the centre of the unit cells is 7 \AA and the radius of the Cs^+ ion is 1.69 \AA , what is the radii of Cl^- ion ?

Sol. $a\sqrt{3} = 7$

$$r_+ + r_- = \frac{a\sqrt{3}}{2} = \frac{7}{2}$$

$$1.69 + r_- = 3.5$$

$$r_- = 3.5 - 1.69 = 1.81 \text{ \AA}$$

Ex.24 In a cubic closed packed structure of mixed oxides the lattice is made up of oxide ions, one eighth of tetrahedral voids are occupied by divalent ions (A^{2+}) while one half of the octahedral voids occupied trivalent ions (B^{3+}). What is the formula of the oxide ?

Sol. Total tetrahedral voids = 8

$$\text{A}^{2+} \text{ occupied} = 8 \times \frac{1}{8} = 1 \text{ tetrahedral void}$$

$$\text{Total octahedral void} = 4$$

$$\text{B}^{3+} \text{ Occupy} = \frac{4}{2} = 2$$

$$\text{A}^{2+} = 1, \text{ B}^{3+} = 2, \text{ O}^{2-} = 4$$

$$\text{formula} = \text{AB}_2\text{O}_4$$

Ex.25 A solid A^+ and B^- has NaCl type closed packed structure. If the anion has a radius of 250 pm , what should be the ideal radius of the cation ? Can a cation C^+ having a radius of 180 pm be slipped into the tetrahedral site of the crystal of A^+B^- ? Give reasons for your answer.

Sol. $\frac{r_+}{r_-} = \sqrt{2} - 1$ for ideal NaCl crystal

$$\frac{r_+}{r_-} = 0.414 \Rightarrow r_- = \frac{r_+}{0.414}$$

$$r_+ = 103.55 \text{ pm}$$

tetrahedral sites

for tetrahedral voids

$$0.225 \leq \frac{r_+}{r_-} < 0.414$$

$$\Rightarrow \frac{r_+}{r_-} = \frac{180}{250} = 0.72$$

no can't slipped

Ex.26 If the radius of Mg^{2+} ion, Cs^+ ion, O^{2-} ion, S^{2-} ion and Cl^- ion are 0.65 \AA , 1.69 \AA , 1.40 \AA , 1.84 \AA , and 1.81 \AA respectively. Calculate the co-ordination numbers of the cations in the crystals of MgS , MgO and CsCl .

Sol. for MgS $\frac{r_+}{r_-} = \frac{0.65}{1.84} = 0.353$

coordination no = 4
tetrahedral void

$$\text{MgO} \Rightarrow \frac{r_+}{r_-} = \frac{0.65}{1.40} = 0.464$$

Octahedral voids
coordination no. = 6

$$\text{CsCl} = \frac{r_+}{r_-} = \frac{1.69}{1.81} = 0.934$$

BCC coordination no. = 8

Ex.27 In a cubic crystal of CsCl (density = 3.97 gm/cm^3) the eight corners are occupied by Cl^- ions with Cs^+ ions at the centre. Calculate the distance between the neighbouring Cs^+ and Cl^- ions.

Sol. $3.94 = \frac{\left(1 \times \frac{M}{N_A}\right)}{a^3} = \frac{168.5}{6.022 \times 10^{23} \times a^3}$

$$\Rightarrow a^3 = \frac{168.5}{6.022 \times 10^{23} \times 3.97}$$

$$a^3 = 7.05 \times 10^{-23} \text{ cm}^3$$

$$a = 4.13 \times 10^{-8} \text{ cm}$$

$$r_+ + r_- = \frac{a\sqrt{3}}{2} = 3.577 \times 10^{-8}$$

$$= 3.577 \times 10^{-10} \text{ cm}$$

$$= 3.577 \text{ \AA}$$

Ex.28 Calculate the value of Avogadro's number from the following data :

Density of NaCl = 2.165 cm^{-3}

Distance between Na^+ and Cl^- in NaCl = 281 pm .

Sol. $d = \frac{ZM}{a^3 N_A}$

$$2.165 = \frac{4 \times 58.5}{(562 \times 10^{-10})^3 N_A}$$

$$\therefore N_A = 6 \times 10^{23}$$

Ex.29 KCl crystallizes in the same type of lattice as does NaCl . Given that $\frac{r_{\text{Na}^+}}{r_{\text{Cl}^-}} = 0.5$ and $\frac{r_{\text{Na}^+}}{r_{\text{K}^+}} = 0.7$

Calculate :

(a) The ratio of the sides of unit cell for KCl to that for NaCl and

(b) The ratio of densities of NaCl to that for KCl

Sol. (a) $\frac{r_{Na^+}}{r_{Cl^-}} = 0.5$, $\frac{r_{K^+}}{r_{Cl^-}} = 0.7$, $\frac{a_{KCl}}{a_{NaCl}} = \frac{2[r_{K^+} + r_{Cl^-}]}{2[r_{Na^+} + r_{Cl^-}]}$ (i)

$$\frac{r_{Na^+}}{r_{Cl^-}} + 1 = 1 + 0.5, \quad \frac{r_{Na^+} + r_{Cl^-}}{r_{Cl^-}} = 1.5 \quad \text{....(ii)}$$

$$\frac{r_{Na^+}}{r_{Cl^-}} \div \frac{r_{K^+}}{r_{Cl^-}} = \frac{5}{7}, \quad \frac{r_{K^+}}{r_{Cl^-}} = \frac{5}{7}, \quad \frac{r_{K^+}}{r_{Cl^-}} + 1 = \frac{5}{7} + 1, \quad \frac{r_{K^+} + r_{Cl^-}}{r_{Cl^-}} = \frac{12}{7} \quad \text{....(iii)}$$

From eq. (i)

$$\frac{a_{KCl}}{a_{NaCl}} = \frac{12/7}{1.5} = \frac{1.714}{1.5} = 1.143$$

(b) $d_{NaCl} = \frac{zM_{NaCl}}{(a_{NaCl})^3 N_A}$, $d_{KCl} = \frac{zM_{KCl}}{(a_{KCl})^3 N_A}$, $\frac{d_{NaCl}}{d_{KCl}} = \frac{M_{NaCl}}{M_{KCl}} \cdot \left(\frac{a_{KCl}}{a_{NaCl}} \right)^3 = \frac{58.5}{74.5} \cdot (1.143)^3 = 1.172$

Ex.30 An element A (Atomic weight = 100) having bcc structure has unit cell edge length 400 pm. Calculate the density of A and number of unit cells and number of atoms in 10 gm of A.

Sol. $a = 400 \text{ pm} = 4 \times 10^{-8} \text{ cm}$
 $z = 2$

$$d = \frac{zM}{a^3 N_A} = \frac{2 \times 100}{(4 \times 10^{-8})^3 \times 6.023 \times 10^{23}} = \frac{200}{38.54} = 5.188 \text{ gm/cc}$$

In 100 gm $\rightarrow 6.023 \times 10^{23}$ atoms

In 10 gm $\rightarrow 6.023 \times 10^{22}$ atoms

Ex.31 The composition of a sample of wustite is $Fe_{0.93}O_{1.0}$. What percentage of iron is present in the form of Fe(III) ?

Sol. Fe : O = 93 : 100
 Let Fe (III) = x
 then Fe (II) = (93 - x)
 Balancing charge, We have
 $x \times 3 + (93 - x) \times 2 = 100 \times 2$
 $x = 200 - 186 = 14$

$$\% \text{ Fe (III)} = \frac{14}{93} \times 100 = 15.05 \%$$

Ex.32 $BaTiO_3$ crystallizes in the perovskite structure. This structure may be described as a cubic lattice with barium ions occupying the corner of the unit cell, oxide ions occupying the face-centers and titanium ion occupying the center of the unit cell.

(a) If titanium is described as occupying holes in BaO lattice, what type of holes does it occupy?

(b) What fraction of this type hole does it occupy ?

Sol. (a) Ti is present at the body centre i.e. it occupies octahedral hole.
 (b) No. of octahedral in c.c.p. = 4

$$\text{Fractional of octahedral hole occupied} = \frac{1}{4}$$

Ex.33 RbI crystallizes in bcc structure in which each Rb^+ is surrounded by eight iodide ions each of radius 2.17 Å. Find the length of one side of RbI unit cell.

Sol. $\frac{r_{\text{Rb}^+}}{r_{\text{I}^-}} = 0.732 \quad \therefore \quad r_{\text{Rb}^+} = 0.732 \times 2.17 = 1.59 \text{ \AA}$

$$a\sqrt{3} = 2[r_{\text{Rb}^+} + r_{\text{I}^-}] \quad a = \frac{2}{\sqrt{3}} [1.59 + 2.17] = 4.34 \text{ \AA}$$

Ex.34 Find the size of largest sphere that will fit in octahedral void in an ideal FCC crystal as a function of atomic radius 'r'. The insertion of this sphere into void does not distort the FCC lattice. Calculate the packing fraction of FCC lattice when all the octahedral voids are filled by this sphere.

Sol. If Radius of sphere is r
 Radius of largest sphere that will fit in the octahedral void is $0.414 r$
 $2[r + 0.414 r] = a$
 $2.828 r = a$

$$\text{Volume of spheres} = 4 \times \frac{4}{3} \pi r^3 + 4 \times \frac{4}{3} \pi (0.414 r)^3 = \frac{16}{3} \pi r^3 [1 + 0.071]$$

$$\text{Volume of unit cell} = a^3 = (2\sqrt{2} r)^3 = 16\sqrt{2} r^3, \quad \phi = \frac{\frac{16}{3} \pi r^3 \times 1.071}{16\sqrt{2} r^3} = \frac{\pi \times 1.071}{3 \times 1.414} = 0.793 \Rightarrow 79.3\%$$

Ex.35 NaH crystallizes in the same structure as that of NaCl. The edge length of the cubic unit cell of NaH is 4.88 Å.

(a) Calculate the ionic radius of H^- , provided the ionic radius of Na^+ is 0.95 Å.

(b) Calculate the density of NaH.

Sol. $a = 4.88 \text{ \AA} = 4.88 \times 10^{-8} \text{ cm}$

$$(a) \quad r_{\text{Na}^+} + r_{\text{H}^-} = \frac{4.88}{2}, \quad r_{\text{H}^-} = 2.44 - 0.95 = 1.49 \text{ \AA}$$

$$(b) \quad d = \frac{ZM}{a^3 N_A} = \frac{4 \times 24}{(4.88 \times 10^{-8})^3 \times 6.023 \times 10^{23}} = 1.37 \text{ gm/cm}^3$$

Ex.36 Metallic gold crystallises in fcc lattice. The length of the cubic unit cell is $a = 4.07 \text{ \AA}$

(a) What is the closest distance between gold atoms.

(b) How many "nearest neighbours" does each gold atom have at the distance calculated in (a).

(c) What is the density of gold?

(d) Prove that the packing fraction of gold is 0.74.

Sol. $a = 4.07 \text{ \AA}$

$$(a) \quad 4r = a\sqrt{2}$$

$$r = \frac{a\sqrt{2}}{4} = \frac{4.07 \times 1.414}{4} = 1.44 \text{ \AA}$$

Closest distance between Au atoms = 2.88 \AA

$$(b) \quad \text{C.N.} = 12$$

$$(c) \quad d = \frac{ZM}{a^3 N_A} = \frac{4 \times 196}{(4.07 \times 10^{-8})^3 \times 6.023 \times 10^{23}} = 19.4 \text{ gm/cc}$$

Ex.37 Graphite in an example of-

(A) Ionic solid

(B) Covalent Solid

(C) Vander waal's Crystal

(D) Metallic crystal

Sol. (B)

Graphite is a covalent solid having sp^2 hybridised carbon atoms.

Ex.38 Which is amorphous solid -

(A) Rubber

(B) Plastic

(C) Glass

(D) All

Sol. (D)

Amorphous solids neither have ordered arrangement (i.e. no definite shape) nor have sharp melting point like crystals, but when heated, they become pliable until they assume the properties usually related to liquid. It is therefore they are regarded as super cooled liquids.

Ex.39 Xenon crystallizes in face centre cubic lattice and the edge of the unit cell is 620 PM, then the radius of Xenon atom is-

(A) 219.20 PM

(B) 438.5 PM

(C) 265.5 PM

(D) 536.94 PM

Sol. (A)

For fcc lattice ; $r = \frac{1}{2\sqrt{2}} \times a$

where $a = 620$ PM

On solving $r = 219.20$ PM.

Ex.40 The edge length of cube is 400 PM. Its body diagonal would be-

(A) 500 PM

(B) 693 PM

(C) 600 PM

(D) 566 PM

Sol. (B)

Since in body centre cubic, the body diagonal

$$= \sqrt{3} a = \sqrt{3} \times 400 \text{ PM} = 692.82 \text{ PM or say } 693 \text{ PM}$$

Ex.41 What is the simplest formula of a solid whose cubic unit cell has the atom A at each corner, the atom B at each face centre and a C atom at the body centre-

(A) AB_2C

(B) A_2BC

(C) AB_3C

(D) ABC_3

Sol. (C)

An atom at the corner of a cube is shared among 8 unit cells. As there are 8 corners in a cube, number of corner atom (A) per unit cell $= 8 \times \frac{1}{8} = 1$.

A face-centered atom in a cube is shared by two unit cells. As there are 6 faces in a cube, number of face-centered atoms (B) per unit cell $= 6 \times \frac{1}{2} = 3$.

An atom in the body of the cube is not shared by other cells.

\therefore Number of atoms (C) at the body centre per unit cell = 1.

Hence, the formula of the solid is AB_3C .

Ex.42 A compound alloy of gold and copper crystallizes in a cube lattice in which the gold atoms occupy the corners of a cube and the copper atoms occupy the centres of each of the cube faces. The formula of this compound is-

(A) AuCu

(B) $AuCu_2$

(C) $AuCu_3$

(D) None

Sol. (C)

One-eighth of each corner atom (Au) and one-half of each face-centered atom (Cu) are contained within the unit cell of the compound.

Thus, the number of Au atoms per unit cell $= 8 \times \frac{1}{8} = 1$ and the number of Cu atoms per unit cell $= 6 \times \frac{1}{2} = 3$. The formula of the compound is $AuCu_3$.

Ex.43 Select the correct statement (s)-

(a) The C.N. of cation occupying a tetrahedral hole is 4.

(b) The C.N. of cation occupying a octahedral hole is 6.

(c) In schottky defects, density of the lattice decreases.

(A) a, b

(B) b, c

(C) a, b, c

(D) a, c

Sol. (C)

Since tetrahedral holes are surrounded by 4 nearest neighbours. So, the C.N. of cation occupying tetrahedral hole is 4. Since octahedral hole is surrounded by six nearest neighbours. So, C.N. of cation occupying octahedral is 6. In schottky a pair of anion and cation leaves the lattice. So, density of lattice decreases.

Ex.44 Lithium borohydride (LiBH_4), crystallises in an orthorhombic system with 4 molecules per unit cell. The unit cell dimensions are : $a = 6.81 \text{ \AA}$, $b = 4.43 \text{ \AA}$, $c = 717 \text{ \AA}$. If the molar mass of LiBH_4 is 21.76 g mol^{-1} . The density of the crystal is-

(A) $.668 \text{ g cm}^{-3}$

(B) $.585 \text{ g cm}^{-3}$

(C) 1.23 g cm^{-3}

(D) None

Sol. (A)

We know that,

$$\rho = \frac{ZM}{NV} ; \text{ where } V = a \times b \times c$$

$$= \frac{4 \times (21.76 \text{ g mol}^{-1})}{(6.023 \times 10^{23} \text{ mol}^{-1}) (6.81 \times 4.43 \times 7.17 \times 10^{-24} \text{ cm}^3)}$$

$$= 0.668 \text{ g cm}^{-3}$$

Ex.45 The unit cell of a metallic element of atomic mass 10^8 and density 10.5 g/cm^3 is a cube with edge length of 409 PM. The structure of the crystal lattice is -

(A) fcc

(B) bcc

(C) hcp

(D) None of these

Sol. (A)

$$\rho = \frac{Z \times M}{N \times a^3}$$

Here, $M = 10^8$, $N_A = 6.023 \times 10^{23}$

Put on these values and solving we get-

$a = 409 \text{ PM} = 4.09 \times 10^{-8} \text{ cm}$,

$\rho = 10.5 \text{ g/cm}^3$

$n = 4$ = number of atoms per unit cell

So, The structure of the crystal lattice is fcc.

Ex.46 Among the following types of voids, which one is the largest void-

(A) Triangular system

(B) Tetragonal system

(C) Monoclinic system

(D) Octahedral

Sol. (D)

The vacant spaces between the spheres in closed packed structure is called void. The voids are of two types, tetrahedral voids and octahedral voids. Also radius of tetrahedral voids and octahedral voids are $r_{\text{void}} = 0.225 \times r_{\text{sphere}}$ and $r_{\text{void}} = 0.411 \times r_{\text{sphere}}$ respectively. Thus, octahedral void is larger than tetrahedral void.

Ex.47 Close packing is maximum in the crystal which is-

(A) Simple cube

(B) bcc

(C) fcc

(D) None of these

Sol. (C)

The close packing in the crystal is 0.52, 0.68 and 0.74 for simple cubic, bcc, and fcc respectively.

i.e the close packing is maximum is fcc.

Ex.48 Bragg's equation is-

(A) $n\lambda = 2\theta \sin \theta$

(B) $n\lambda = 2d \sin \theta$

(C) $2n\lambda = d \sin \theta$

(D) $\lambda = (2d/n) \sin \theta$

Sol. (B)

Bragg's equation is $n\lambda = 2d \sin \theta$.

Ex.49 Copper metal has a face-centred cubic structure with the unit cell length equal to 0.361 nm. Picturing copper ions in contact along the face diagonal, The apparent radius of a copper ion is-

- (A) 0.128 (B) 1.42 (C) 3.22 (D) 4.22

Sol. (A)

For a face-centred cube, we have,

$$\text{radius} = \frac{\sqrt{2} a}{4} = \frac{\sqrt{2} \times 0.361}{4} \text{ nm} = 0.128.$$

Ex.50 The rank of a cubic unit cell is 4. The type of cell as-

- (A) Body centred (B) Face centred (C) Primitive (D) None

Sol. (B)

The number of atoms present in sc, fcc and bcc unit cell are 1, 4, 2 respectively.

Ex.51 At room temperature, sodium crystallises in a body centred cubic cell with $a = 4.24 \text{ \AA}$. The theoretical density of sodium is -(Atomic mass of sodium = 23.0 g mol^{-1})

- (A) 2.05 g cm^{-3} (B) 3.45 g cm^{-3} (C) 1.00 g cm^{-3} (D) 3.55 g cm^{-3}

Sol. (C)

The value of Z for a bcc unit cell is 2.

$$\text{Volume } V = (4.24 \text{ \AA})^3$$

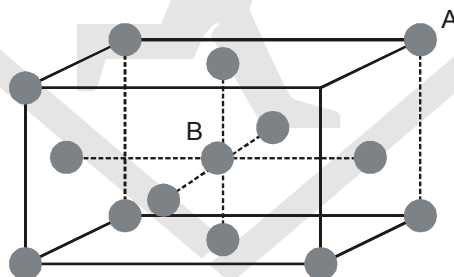
$$\therefore \rho = \frac{ZM}{NV} = \frac{2 \times 23}{(6.023 \times 10^{23}) \times (4.24 \times 10^{-8})^3}$$

$$= 1.00 \text{ g / cm}^3$$

Solved Subjective Problems

Ex.1 A face-centred cubic solid of an element A has a largest sized guest atom B at the body centre octahedral hole if insertion of B doesn't affect the original unit cell dimension; determine the packing fraction of the solid.

Sol. In the given solid, there is one B and four A per unit cell.



Also, under the condition of largest possible size of B, it will be in contact of A present at the face centres only and the following relationship will exist :

$$4r_A = \sqrt{2} a \quad \text{and} \quad 2(r_A + r_B) = a$$

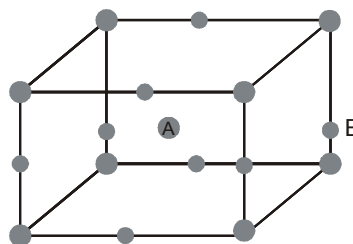
$$\text{solving} \quad \frac{r_B}{r_A} = 0.414$$

Now, packing fraction

$$(\phi) = \frac{4\pi}{3} (4r_A^3 + r_B^3) \times \frac{1}{a^3} = \frac{4\pi}{3} (4r_A^3 + r_B^3) \times \frac{1}{1\sqrt{2}r_A^3}$$

$$= \frac{\pi}{12\sqrt{2}} \left[4 + \left(\frac{r_B}{r_A} \right)^3 \right] = \frac{\pi}{12\sqrt{2}} [4 + (0.414)^3] = 0.7536$$

Ex.2 An element A has BCC structure and another guest atom B, of largest possible size are present at each edge centres of unit cell of A but without disturbing the original unit cell dimension. Determining the void percentage of this solid.



Sol. Since B is closer to corner than to face centre, in close contact,

$$2(r_A + r_B) = a$$

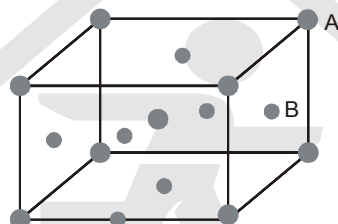
$$4r_A = \sqrt{3}a \quad \Rightarrow \quad \frac{r_B}{r_A} = 0.155$$

In a unit cell, there are two A and $12 \times \frac{1}{4} = 3B$

$$\Rightarrow \text{Packing fraction } (\phi) = \frac{4\pi}{3}(2r_A^3 + 3r_B^3) \times \frac{1}{a^3}$$

$$= \frac{\sqrt{3}\pi}{16} \left[2 + 3 \left(\frac{r_B}{r_A} \right)^3 \right] = 0.684 \quad \Rightarrow \text{Void space} = 31.6\%$$

Ex.3 An element A has a BCC structure and another guest atoms B, of largest possible size, are present at the face centres, but without disturbing the unit cell dimension. Determine the packing fraction of this solid.



Sol. In the above solid, face centres are closer to body centre, therefore, the relationship.

$$2(r_A + r_B) = 0$$

$$4r_A = \sqrt{3}a \quad \Rightarrow \quad \frac{r_B}{r_A} = 0.155$$

$$\text{Now, packing fraction } (\phi) = \frac{4\pi}{3}(2r_A^3 + 3r_B^3) \times \frac{1}{a^3} = \frac{\sqrt{3}\pi}{16} \left[2 + 3 \left(\frac{r_B}{r_A} \right)^3 \right] = 0.684$$

Ex.4 Calcium has face-centred cubic lattice and radius of calcium atom is 195.6 picometre. Determine the number of Ca atoms present on surfaces of a mm^3 block of calcium metal assuming that atoms are in the closest packing.

Sol. In FCC, the relation is

$$4r = \sqrt{2}a \quad \Rightarrow \quad a = 2\sqrt{2}r = 553.24 \times 10^{-9} \text{ mm.}$$

$$\Rightarrow \text{Area of a face of unit cell} = a^2 = 3.06 \times 10^{-13} \text{ mm}^2$$

$$\Rightarrow \text{Surface area of metal block} = 6 \text{ mm}^2$$

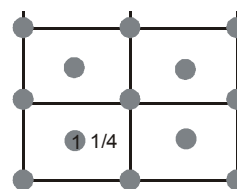
$$\Rightarrow \text{Total number of faces of unit cells present on surface}$$

$$= \frac{6}{3.06 \times 10^{-13}} = 1.96 \times 10^{13}$$

Each face contributes two Ca atoms on surface as shown in diagram.

$$\Rightarrow \text{Total number of Ca atoms present on surface}$$

$$= 2 \times 1.96 \times 10^{13} = 3.92 \times 10^{13}$$



Ex.5 An atom crystallises in hexagonal closed pack arrangement. Determine dimensions (radius and length) of a large cylindrical atom that can be accommodated in the centre of HCP, in terms of radius of host atom.

Sol. The cylinder will pass through centre of middle layer and will lie between the face centres.

Therefore,

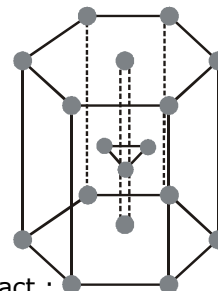
Height of cylinder (h) = height of hexagon (h) = $2r$

Since, in HCP : $H = 4\sqrt{\frac{2}{3}}r$, where r = radius of atoms.

$$\Rightarrow h = \left(4\sqrt{\frac{2}{3}} - 2\right) r = 1.266 r$$

Also, if R is the radius of cylinder, then in the case of closet contact :

$$\frac{R}{r} = 0.155 \Rightarrow R = 0.155 r, \Rightarrow h = 1.266 r$$



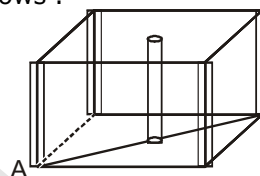
Ex.6 A uniform cylindrical, polymer molecule crystallizes in body centred cubic array. Determine the packing fraction of this polymer in solid state assuming that molecules are in their closest contact.

Sol. The arrangement of molecules can be represented as follows :

$$\text{Here, } 4r = \sqrt{2}l \Rightarrow l = 2\sqrt{2}r$$

$$\text{Packing fraction } (\phi) = \frac{2\pi r^2 l}{l^3} = \frac{2\pi r^2}{l^2}$$

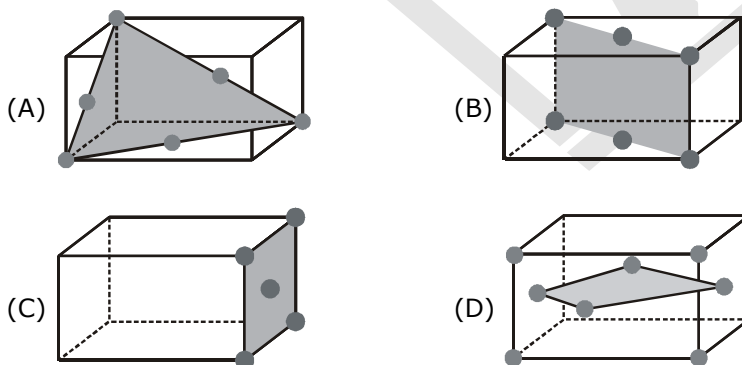
$$= \frac{\pi}{4} = 0.785$$



Ex.7 Show the following arrays of atoms on a plane in an atomic FCC.



Sol.



Ex.8 Cesium bromide crystallizes in cubic arrangement like CsCl. Given the ionic radii of Cs^+ and Br^- are 1.88 \AA and 1.82 \AA respectively, determine the packing fraction.

Sol. Here Cs^+ ion is at body centre and Br^- at the corners, therefore the relationship is

$$2(r_+ + r_-) = \sqrt{3}a = 2(1.88 + 1.82) \text{ \AA}, \Rightarrow a = 4.27 \text{ \AA}$$

$$\text{Packing fraction } (\phi) = \frac{4}{3}\pi \left(\frac{r_+^3 + r_-^3}{a^3} \right) = \frac{4}{3}\pi \left(\frac{(1.88)^3 + (1.82)^3}{(4.27)^3} \right) = 0.6807$$

Ex.9 Titanium metal crystallises in a BCC arrangement and radius of an atom is 142 picometre. Determine atomic weight of titanium if density is 16.6 g/cm³. Also determine the number of unit cells present in a 5 cm³ block of titanium metals.

Sol. In BCC arrangement of atoms the relationship between edge length radius of atom is

$$4r = \sqrt{3}a$$

$$\text{Density } (\rho) = \frac{NM}{N_A V}$$

Where, N = Number of atoms per unit cell,

M = Molar mass, N_A = Avogadro's number

V = Volume of unit cell

$$\Rightarrow 16.6 = \frac{2M}{6.023 \times 10^{23} \left(\frac{4}{\sqrt{3}} \times 142 \times 10^{-10} \right)^3}$$

Here, radius is taken in cm unit since, density is in g/cm³ unit.

Solving : M = 176. Also mass of 5 cm³ block = 5 × 16.6 = 83 g

$$\Rightarrow \text{Number of atoms in } 5 \text{ cm}^3 \text{ block} = \frac{83}{176} \times 6.023 \times 10^{23}$$

$$\Rightarrow \text{Number of unit cells} = \frac{\text{No. of atoms}}{2} = \frac{83 \times 6.23 \times 10^{23}}{176 \times 2} = 1.42 \times 10^{23}$$

Ex.10 Copper metal crystallizes in face-centred cubic arrangement and surface of adjacent atoms along the edge of unit cell are 106 picometre apart. Determine the density of metal. Atomic mass of copper metal is 63.5 u.

Sol. According to the given information, a view of one face of the unit cell will be as shown below.

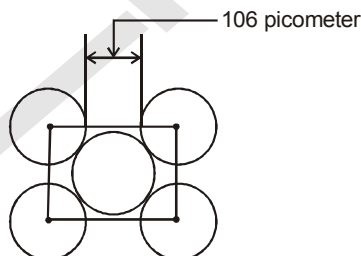
In FCC; $4\sqrt{2}a$

The given distance is $a - 2r = a - \frac{a}{\sqrt{2}}$

$$= a \left[\frac{\sqrt{2} - 1}{\sqrt{2}} \right] = 106 \text{ pm}$$

$$\Rightarrow a = 362 \text{ pm} = 3.62 \times 10^{-8} \text{ cm}$$

$$\Rightarrow \text{Density } (\rho) = \frac{4 \times 63.5}{6.023 \times 10^{23} (3.62 \times 10^{-8})^3} = 8.89 \text{ g/cm}^3$$



Ex.11 Potassium crystallizes in "body centred cubic" arrangement and the surfaces of adjacent atom along the edges of unit cells are 71.4 picometre apart. Determine the density of metal. Atomic weight of K = 39.

Sol. In BCC, the relationship between edge length and radius of atom is

$$4r = \sqrt{3}a$$

Also, given $a - 2r = 71.4 \times 10^{-10} \text{ cm}$

$$\Rightarrow a - \frac{\sqrt{3}}{2}a = a \left[\frac{2 - \sqrt{3}}{2} \right] = 71.4 \times 10^{-10} \text{ cm}$$

$$\Rightarrow a = 5.329 \times 10^{-10} \text{ cm}$$

$$\Rightarrow \text{Density } (\rho) = \frac{2 \times 39}{6.023 \times 10^{23} (5.329 \times 10^{-8})^3} = 0.855 \text{ g/cm}^3$$

Ex.12 Magnesium oxide has the NaCl structure and radii of Mg^{2+} and O^{2-} ions are 0.86 Å and 1.24 Å. Determine the density of magnesium oxide solid.

Sol. In a unit cell, there are four unit of MgO and edge-length of the unit cell is
 $a = 2 (\text{radius of cation} + \text{radius of anion})$
 $= 2 (0.86 + 1.24) = 4.2 \text{ Å}$

$$\text{Density } (\rho) = \frac{4 \times 40}{6.023 \times 10^{23} (4.2 \times 10^{-8})^3} = 3.585 \text{ g/cc}$$

Ex.13 An unknown substance that uses gas at room temperature can be condensed to a solid at -80°C . As a solid, it is found to have cubic unit cell, 5.15 Å on each side, containing four molecules. The density of solid is 0.73 g/cm³. What is the density of the substance as a gas at 27°C and at a pressure of 1.00 atmosphere?

Sol. For a cubic unit cell :

$$\text{Density } (\rho) = \frac{nM}{N_A a^3}$$

Where, n : No. of molecules per unit cell,

M = Molar mass

N_A = Avogadro's constant,

a = Edge length of unit cell.

$$\Rightarrow 0.73 \text{ g/cm}^3 = \frac{4 \times M}{6.023 \times 10^{23} (5.15 \times 10^{-6} \text{ cm})^3}$$

$$M = 15 \text{ g/mol}$$

Molar mass of a substance is independent of state.

$$\Rightarrow \text{As a gas, Density } (\rho) = \frac{pM}{RT} = \frac{1.05 \times 15}{0.082 \times 300} = 0.6097 \text{ g/L.}$$

Ex.14 Aluminium crystallizes in a cubic lattice with an edge of 404 pm and density of metal is 2.70 g/cm³. What type of cubic is formed by aluminium?

Sol. If there is "n" aluminium atoms per unit cell :

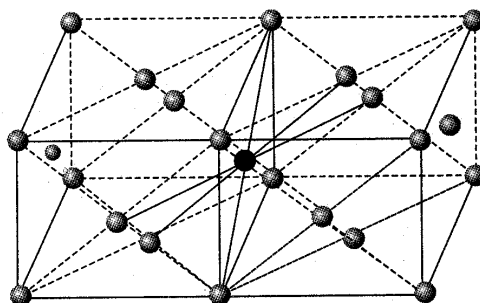
$$\text{Density } (\rho) = \frac{nM}{N_A a^3}$$

$$\Rightarrow 2.70 = \frac{n \times 270}{6.023 \times 10^{23} (4.04 \times 10^{-8} \text{ cm})^3}$$

$$\Rightarrow n = 6.023 \times 10^{22} (4.04 \times 10^{-8})^{-3} = 3097 \approx 4$$

Hence, Al forms face-centred cubic (FCC) lattice.

the coordination number of Al in FCC is 12 i.e., each Al atom has twelve other Al atoms in its nearest neighbour.



An atom of aluminium (solid black) present on the centre of middle vertical face is equidistant from the twelve adjoining atoms, hence, coordination number of an atom in FCC arrangement is twelve.

Ex.15 Except helium, all the noble gases crystallize with cubic close packed structures. Derive an equation relating atomic radius to the density of cubic close packed solid of given mass and apply it to deduce the relative size of Ar and Xe if their densities are 1.4 g/cm and 2.83 g/cm³ respectively.

Sol. For a CCP solid : $\rho = \frac{nM}{N_A a^3}$

Where, ρ = Density, n = No. of atoms/unit cell
 M = Molar mass, N_A = Avogadro constant,
 and a = Edge length

$$\Rightarrow \rho = \frac{4M}{N_A (2\sqrt{2}r)^3} = \frac{M}{4\sqrt{2}N_A r^3} \Rightarrow \frac{\rho_{Xe}}{\rho_{Ar}} = \frac{2.83}{1.40} = \frac{131}{40} \left(\frac{r_{Ar}}{r_{Xe}} \right)^3 \Rightarrow \frac{r_{Xe}}{r_{Ar}} = \left(\frac{131 \times 1.4}{40 \times 2.83} \right)^{1/3} = 1.174$$

Ex.16 All alkali metals crystallize into BCC structures.

(a) Find an equation relating the metallic radius to the density of a BCC solid in terms of its molar mass.

(b) Determine the relative size of Cs atom compared to a Li atom, if their densities are 1.87 g/cc and 0.53 g/cc, respectively.

Sol. (a) For a BCC solid of an element, there are two atoms per unit cell.

$$\Rightarrow \text{Density } (\rho) = \frac{2 \times M}{6.023 \times 10^{23} a^3}$$

Also; in BCC of an atomic solid,

$$\rho = \frac{2M \times 3\sqrt{3}}{6.023 \times 10^{23} \times 64r^3} = 2.696 \times 10^{-23} \frac{M}{r^3}$$

$$(b) \frac{\rho_{Cs}}{\rho_{Li}} = \frac{1.87}{0.53} = \frac{133}{7} \left(\frac{r_{Li}}{r_{Cs}} \right)^3$$

$$\Rightarrow \frac{r_{Cs}}{r_{Li}} = 1.753 \Rightarrow r_{Cs} = 1.753 r_{Li}$$

Ex.17 Some of the metals with BCC structures are not close packed. Therefore, their densities would be greater if they were to change to a cubic close packed structure. What would be density of a metal if it had a cubic close packed structure rather than BCC? Its actual density is 19.3 g/cc.

Sol. $\rho_{CCP} = \frac{4M}{N_A a_{CCP}^3}$ and $\rho_{BCC} = \frac{2M}{N_A a_{BCC}^3}$, $\Rightarrow \frac{\rho_{CCP}}{\rho_{BCC}} = 2 \left(\frac{a_{BCC}}{a_{CCP}} \right)^3$: Also in FCC $4r = \sqrt{2} a_{CCP}$

in BCC, $4r = \sqrt{3} a_{BCC}$

$$\Rightarrow \frac{\rho_{CCP}}{19.3} = 2 \left(\frac{2}{3} \right)^{3/2} = 1.08867 \Rightarrow \rho_{CCP} = 21 \text{ g/cc}$$

Ex.18 How many unit cells of KBr are present in a 1.00 mm³ of KBr, KBr crystallizes in NaCl type of crystal lattice and its density is 2.75 g/cm³.

Sol. In a unit cell of KBr, there are four formula units of KBr.

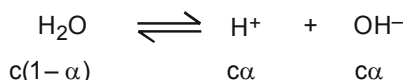
$$\text{Therefore, density } (\rho) = \frac{4 \times 119}{6.023 \times 10^{23} \times a^3} = 2.75, \Rightarrow a^3 = 2.778 \times 10^{-22} \text{ cm}^3 = 2.778 \times 10^{-19} \text{ mm}^3$$

$$\Rightarrow \text{No. of unit cells per mm}^3 = \frac{10^{19}}{2.778} = 3.6 \times 10^{18}$$

Solved Example

Ex.1 At 25°C the degree of ionization of water was found to be 1.8×10^{-9} . Calculate the ionization constant and ionic product of water at this temperature

Sol. If α is the degree of ionization of water, then



$$c = [\text{H}_2\text{O}] = \frac{1000}{18} = 55.56 \text{ M}$$

$$K_{\text{eq}} = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \frac{(c\alpha)^2}{c(1-\alpha)} = c\alpha^2 \quad (\text{since } \alpha \text{ is very much less than } 1)$$

$$K_{\text{eq}} = 55.56 \times (1.8 \times 10^{-9})^2 = 1.8 \times 10^{-16} \text{ M}$$

$$K_w = [\text{H}^+][\text{OH}^-] = (c\alpha)^2 = (55.56 \times 1.8 \times 10^{-9})^2$$

$$K_w = 1.0 \times 10^{-14} \text{ M}^2$$

Ex.2 (a) Calculate the pH of a 0.01 M solution of benzoic acid, the K_a being 7.3×10^{-5} .

(b) 0.2 M solution of $\text{Ba}(\text{OH})_2$ is found to be 90% ionised at 25°C. Find the pH of the solution at that temperature.

Sol. (a) First calculate α using the expression, $\alpha =$

$$\sqrt{\frac{K_a}{c}} = \sqrt{\frac{7.3 \times 10^{-5}}{0.01}} = 0.085$$

$$\text{pH} = \frac{1}{2}(\text{p}K_a - \log c) = \frac{1}{2}(4.13 - 0.01) = 2.06$$

$$(b) [\text{OH}^-] = 0.2 \times 0.9 \times 2 = 0.36$$

$$\text{pOH} = 0.44; \text{pH} = 13.56$$

Ex.3 What is the pH of a 1.0M solution of acetic acid? To what volume must 1 litre of the solution be diluted so that the pH of the resulting solution will be twice the original value? Given: $K_a = 1.8 \times 10^{-5}$.

Sol. Let us first calculate α using $\alpha = \sqrt{\frac{K_a}{c}}$

$$\alpha = \sqrt{\frac{1.8 \times 10^{-5}}{1}} = 4.24 \times 10^{-3}$$

Since, α is very much smaller than 0.1, so the assumption is valid

$$\therefore [\text{H}^+] = \alpha = 2.19 \times 10^{-5}$$

$$\therefore [\text{H}^+] = \sqrt{K_a \times c} = \sqrt{1.8 \times 10^{-5} \times 1} = 4.24 \times 10^{-3}$$

$$\text{pH} = -\log(4.24 \times 10^{-3}) = 3 - \log 424 = 3 - 0.6273 = 2.37$$

$$\text{Now pH on dilution} = 2 \times 2.37 = 4.74$$

$$[\text{H}^+] = 1.8 \times 10^{-5} = c\alpha$$

$$K_a = \frac{c\alpha^2}{1-\alpha} = \frac{c\alpha \times \alpha}{1-\alpha} = \frac{1.8 \times 10^{-5} \times \alpha}{1-\alpha} = 1.8 \times 10^{-5}$$

$$\frac{\alpha}{1-\alpha} = 1 \quad \therefore \alpha = 0.5$$

$$[\text{H}^+] = ac$$

$$c = \frac{[\text{H}^+]}{\alpha} = \frac{1.8 \times 10^{-5}}{0.5} = 3.6 \times 10^{-5} \text{ M}$$

Let the volume to which 1 l of 1 M acetic acid is diluted be V, then

$$1 \times 1 = 3.6 \times 10^{-5} \times V$$

$$V = \frac{1 \times 1}{3.6 \times 10^{-5}} = \frac{10^5}{3.6} = 0.277 \times 10^4 \text{ litres.}$$

You can notice that α increases on dilution and it becomes considerable and cannot be ignored with respect to 1.

Ex.4 A weak base, BOH is titrated with a strong acid HA. When 10 ml of HA is added, the pH of the solution is 10.2 and when 25 ml is added, the pH of the solution is 9.1. Calculate the volume of acid that would be required to reach equivalence point.

Sol. Let the molarity of HA be ' M_2 ' and the molarity and volume of weak base (BOH) are M_1 and V_1 respectively.

In first case,



$$\begin{array}{ccccccc} \text{mmole before reaction} & M_1V_1 & 10M_2 & 0 & 0 & & \\ & (M_1V_1 - 10M_2) & 0 & 10M_2 & 10M_2 & & \end{array}$$

Since the solution (after addition of 10 ml of HA) contains weak base (BOH) and salt of its conjugate base (BA), the solution behaves like a basic buffer.

$$\therefore \text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \quad 14 - 10.2 = \text{p}K_b + \log \frac{10M_2}{(M_1V_1 - 10M_2)}$$

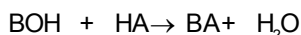
Dividing numerator and denominator of log term by M_2 gives

$$\begin{aligned} 3.8 &= \text{p}K_b + \log \frac{10M_2}{M_2} \\ \therefore 3.8 &= \text{p}K_b + \log \left(\frac{M_1V_1}{M_2} - \frac{10M_2}{M_2} \right) \end{aligned}$$

$$3.8 = \text{p}K_b + \log \frac{10}{V_2 - 10} \quad \dots(i)$$

where V_2 is the volume of acid required to get equivalence point (At equivalence point, $M_1V_1 = M_2V_2$)

In second case,



mmole before reaction M_1V_1 $25M_2$ 0 0

mmole after reaction ($M_1V_1 - 25M_2$) 0 $25M_2$ $25M_2$

$$14 - 9.1 = 4.9 = \text{p}K_b + \log \frac{25M_2}{(M_1V_1 - 25M_2)}$$

Dividing numerator and denominator of log term by M_2

$$4.9 = \text{p}K_b + \log \frac{25}{V_2 - 25} \quad \dots(ii)$$

Subtracting equation (i) from (ii)

$$4.9 - 3.8 = 1.1 = \left(\log \frac{25}{V_2 - 25} \right) - \left(\log \frac{10}{V_2 - 10} \right)$$

$$\text{Taking antilog, } 12.58 = \frac{5V_2 - 50}{2V_2 - 50} \therefore V_2 = 28.72 \text{ ml}$$

Ex.5 20 ml of 0.2 M NaOH is added to 50 ml of 0.2 M acetic acid. What is the pH of the resulting solution? Calculate the additional volume of 0.2 M NaOH required making the solution of pH 4.74. The ionization constant of acetic acid is 1.8×10^{-5} .

Sol. 20 ml of 0.2 M NaOH would react with 20 ml of 0.2 M acetic acid.

$$[\text{Acid}] = 30 \text{ ml of } 0.2 \text{ M present in } 70 \text{ ml} = \frac{30 \times 0.2}{70} = \frac{6}{70} \text{ mole}$$

$$[\text{Salt}] = 20 \text{ ml of } 0.2 \text{ M present in } 70 \text{ ml} = \frac{20 \times 0.2}{70} = \frac{6}{70} \text{ mole}$$

$$\text{p}K_a = -\log 1.8 \times 10^{-5} = 4.74$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{Acid}]} = 4.74 + \log \frac{4}{70} \times \frac{70}{6}$$

$$\text{pH} = 4.74 + \log 0.66 = 4.74 - 0.18 = 4.56$$

To make a solution of pH = 4.74, $[\text{Acid}] = [\text{Salt}]$

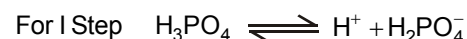
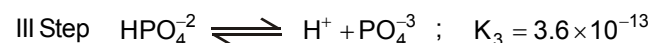
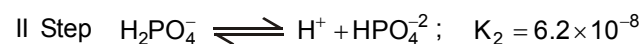
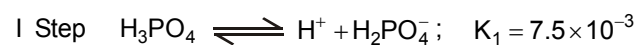
So 25 ml of 0.2 M NaOH must be added to 50 ml of 0.2 M acetic acid.

Addition volume of NaOH to be added = $25 - 20 = 5 \text{ ml}$

Ex.6 Calculate the concentrations of all the species present in 0.1 M H_3PO_4 solution.

Given : $K_1 = 7.5 \times 10^{-3}$, $K_2 = 6.2 \times 10^{-8}$ and $K_3 = 3.6 \times 10^{-13}$.

Sol.



$$\begin{array}{ccc} 0.1 \text{ M} & 0 & 0 \\ (0.1 - c) \text{ M} & c & c \end{array}$$

$$K_1 = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = \frac{c^2}{(0.1 - c)} \quad 7.5 \times 10^{-3} = \frac{c^2}{(0.1 - c)}$$

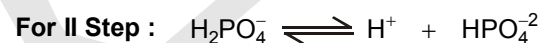
Solving the quadratic equation,

$$c = 0.024$$

$$\therefore [\text{H}^+] = 0.024 \text{ M} \quad \therefore [\text{H}_2\text{PO}_4^-] = 0.024 \text{ M}$$

$$[\text{H}_3\text{PO}_4] = 0.024 \text{ M} \quad [\text{H}_3\text{PO}_4] = 0.1 - 0.024 = 0.076 \text{ M}$$

The value of K_1 is much larger than K_2 and K_3 . Also dissociation of II and III steps occurs in presence of H^+ furnished in I step and thus, dissociation of II and III steps is further suppressed due to common ion effect.



$$\begin{array}{ccc} 0.024 & 0.024 & 0 \\ (0.024 - y) & (0.024 + y) & y \end{array}$$

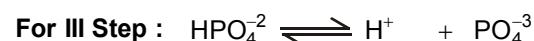
The dissociation of H_2PO_4^- occurs in presence of $[\text{H}^+]$ furnished in step I.

$$\text{Thus, } K_2 = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \text{ or } 6.2 \times 10^{-8} = \frac{(0.024 + y)y}{(0.024 - y)}$$

$$\therefore y \text{ is small } \therefore 0.024 - y \approx 0.024 \text{ and neglecting } y^2.$$

$$\therefore 6.2 \times 10^{-8} = \frac{0.024 y}{0.024} \quad \therefore y = 6.2 \times 10^{-8}$$

$$\text{or } [\text{HPO}_4^{2-}] = K_2 = 6.2 \times 10^{-8} \text{ M}$$



$$(6.2 \times 10^{-8} - x) \quad (0.024 + x) \quad x$$

$$K_3 = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = \frac{(0.024 + x) \cdot x}{(6.2 \times 10^{-8} - x)}$$

Again neglecting x^2 and assuming, $6.2 \times 10^{-8} - x = 6.2 \times 10^{-8}$

$$\therefore 3.6 \times 10^{-13} = \frac{0.024 x}{6.2 \times 10^{-8}}$$

$$\therefore [PO_4^{3-}] = x = \frac{3.6 \times 10^{-13} \times 6.2 \times 10^{-8}}{0.024} = 9.3 \times 10^{-19} \text{ M.}$$

Ex.7 The pH of blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentrations. What volume of 5 M $NaHCO_3$ solution, should be mixed with 10 ml sample of blood, which is 2 M in H_2CO_3 in order to maintain a pH of 7.4 K_a for H_2CO_3 in blood is 7.8×10^{-7} ?

Sol. Let the volume of 5 M $NaHCO_3$ solution added be x ml.

Number of millimoles of $NaHCO_3 = 5x$

Number of millimoles of $H_2CO_3 = 10 \times 2 = 20$

For the acidic buffer, $pH = pK_a + \log \frac{[NaHCO_3]}{[H_2CO_3]}$

$$7.4 = -\log(7.8 \times 10^{-7}) + \log \frac{5x}{20}$$

On solving, $x = 78.37$ ml

\therefore Volume of $NaHCO_3$ solution required = 78.37 ml.

Ex.8 An indicator is a weak acid and the pH range of its colour is 3.1 to 4.5. If the neutral point of the indicator lies in the center of the hydrogen ion concentrations corresponding to the given pH range, calculate the ionization constant of the indicator.

Sol. The hydrogen ion concentrations of the given pH range are

For pH 3.1, $pH = -\log [H^+] = 3.1$

$[H^+] = 7.94 \times 10^{-4} \text{ M}$ For pH 4.5,

$pH = 4.5 = -\log [H^+] \therefore [H^+] = 3.16 \times 10^{-5} \text{ M}$

The average of these two hydrogen ion concentrations is

$$\frac{(7.9 \times 10^{-4}) + (3.16 \times 10^{-5})}{2} = 4.128 \times 10^{-4} \text{ M}$$

At this concentration of H^+ , we will get neutral point of the indicator, at which $[In^-] = [HIn]$

$\therefore pH = pK_{HIn}$

or $[H^+] = K_{HIn} = 4.128 \times 10^{-4}$

Ex.9 Calcium lactate is a salt of a weak organic acid and is represented as $Ca(Lac)_2$. A saturated solution of $Ca(Lac)_2$ contains 0.13 mol of this salt in 0.5 litre solution. The pOH of this solution is 5.6. Assuming complete dissociation of the salt, calculate K_a for lactic acid.

Sol. $Ca(Lac)_2(s) \rightarrow Ca(Lac)_2(aq) \rightarrow Ca^{2+}(aq) + 2Lac^-(aq)$



Since it is salt of strong base and weak acid, its pH is calculated as

$$pH = \frac{1}{2}[pK_w + pK_a + \log c] \quad pH = 14 - pOH = 14 - 5.6 = 8.4$$

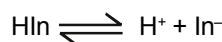
$$8.4 = \frac{1}{2}[14 + pK_a + \log 0.52] \quad (\therefore c = 2 \times 0.13/0.5)$$

$$pK_a = (2 \times 8.4) - 14 - \log 0.52 = 3.08$$

$$\therefore K_a = 8.31 \times 10^{-4}$$

Ex.10 A certain acid - base indicator is red in acid and blue in basic solution. At pH = 5, 75% of the indicator is present in the solution in its blue form. Calculate dissociation constant (K_a) for the indicator and pH range over which the indicator changes from 90% red-10% blue to 90% blue-10% red.

Sol. Since K_a is asked, the indicator must be an acid. Let the acid be represented by HIn .



In acid solution, the indicator will be predominately present in the form of HIn (due to common ion effect.) Since in acid solution the colour is red, this would be due to HIn . In basic solution, the indicator will be predominately in the form of In^- . Since the indicator is blue in basic solution, so In^- must be blue in colour.

At pH = 5, the indicator is 75% blue. This also means it is 25% red.

$$\therefore K_a = \frac{10^{-5} \times 0.75}{0.25} = 3 \times 10^{-5}$$

pH when it is 90% red & 10% blue

$$\therefore [H^+] = \frac{K_a \times [HIn]}{[In^-]} = \frac{3 \times 10^{-5} \times 0.9}{0.1} = 2.7 \times 10^{-4}$$

$$\therefore pH = 3.56$$

pH when it is 90% blue and 10% red :

$$[H^+] = \frac{K_a \times [HIn]}{[In^-]} = \frac{3 \times 10^{-5} \times 0.1}{0.9} = 3.3 \times 10^{-6}$$

Ex.11 Determine the number of mole of AgI which may be dissolved in 1.0 litre of 1.0 M CN⁻ solution.

Given K_{sp} for AgI and K_c for $\text{Ag}(\text{CN})_2^-$ are $1.2 \times 10^{-17} \text{ M}^2$ and $7.1 \times 10^{19} \text{ M}^{-2}$ respectively.

Sol. Given, $\text{AgI(s)} \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{I}^-(\text{aq})$

$$; K_{sp} = [\text{Ag}^+][\text{I}^-] = 1.2 \times 10^{-17} \quad \dots(\text{i})$$



$$; K_f = \frac{[\text{Ag}(\text{CN})_2^-]}{[\text{Ag}^+][\text{CN}^-]^2} = 7.1 \times 10^{19} \quad \dots(\text{ii})$$

Let 'x' mole of AgI be dissolved in CN⁻ solution, then



Mole before reaction

$$1 \quad 0 \quad 0$$

Mole at equilibrium $(1 - 2x) \quad x \quad x$

By equations (i) and (ii). $K_{eq} = K_{sp} \times K_f$

$$K_{eq} = \frac{[\text{Ag}(\text{CN})_2^-][\text{I}^-]}{[\text{CN}^-]^2} = 1.2 \times 10^{-17} \times 7.1 \times 10^{19}$$

$$K_{eq} = 8.52 \times 10^2 \quad \dots(\text{iii})$$

$$\therefore K_{eq} = 8.52 \times 10^2 = \frac{x^2}{(1-2x)^2} \quad \text{or} \quad \frac{x}{1-2x} = 29.2$$

$$\therefore x = 0.49 \text{ mole.}$$

Ex.12 The solubility product of calcium oxalate is 2×10^{-9} at 25°C. Calculate the solubility of calcium oxalate at this temperature. What will be its solubility in a 0.1 M solution of ammonium oxalate? Assume that ammonium oxalate is completely ionized in solution. Name the effect, which operates on addition of ammonium oxalate to calcium oxalate.

Sol. The solubility product, K_{sp} of calcium oxalate is given by

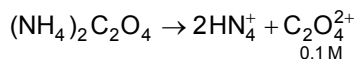
$$K_{sp} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = 2 \times 10^{-9}$$

Let 's' be the solubility of calcium oxalate in mole litre⁻¹.

$$s^2 = 2 \times 10^{-9}$$

$$s = \sqrt{2 \times 10^{-9}} = 4.472 \times 10^{-5} \text{ mole/l.}$$

Let the solubility of CaC_2O_4 be s' in the presence of 0.1 M ammonium oxalate solution.



Since CaC_2O_4 is sparingly soluble, the concentration of $\text{C}_2\text{O}_4^{2-}$ derived from CaC_2O_4 is negligible in comparison to 0.1.

$$K_{sp} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = s' \times 0.1 = 2 \times 10^{-9}$$

$$s' = \frac{2 \times 10^{-9}}{0.1} = 2 \times 10^{-8} \text{ mole/l.}$$

In the presence of ammonium oxalate, the solubility of CaC_2O_4 drops from 4.472×10^{-5} to 2×10^{-8} mole/l. This effect is called common-ion effect.

Ex.13 At 25°C, will a precipitate of $\text{Mg}(\text{OH})_2$ form in a $1 \times 10^{-4} \text{ M}$ solution of $\text{Mg}(\text{NO}_3)_2$ if pH of the solution is adjusted to 9.0. [$K_{sp}(\text{Mg}(\text{OH})_2) = 8.9 \times 10^{-12} \text{ M}^3$]. At which minimum pH will the precipitation start?

Sol. If pH = 9.0, $[\text{H}^+] = 1 \times 10^{-9} \text{ M}$, then

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1 \times 10^{-14}}{1 \times 10^{-9}} = 1 \times 10^{-5} \text{ M}$$

The ionic product of $\text{Mg}(\text{OH})_2$ in the solution would be

$$[\text{Mg}^{2+}][\text{OH}^-]^2 = (1 \times 10^{-4})(1 \times 10^{-5})^2 = 1 \times 10^{-14} \text{ M}^3$$

Since, the value of ionic product is smaller than

$K_{sp}(8.9 \times 10^{-12})$, so no precipitate of $\text{Mg}(\text{OH})_2$ will be formed.

The minimum concentration of OH^- needed to precipitate Mg^{2+} from the solution is

$$[\text{OH}^-] = \sqrt{\frac{K_{sp}}{[\text{Mg}^{2+}]}} = \sqrt{\frac{8.9 \times 10^{-12}}{1 \times 10^{-4}}} = 2.98 \times 10^{-4} \text{ M}$$

$$\therefore \text{Maximum pOH} = 3.54$$

$$\text{and minimum pH} = 14 - 3.54 = 10.46$$

Class Room Problems

Ex.1 Nicotinic acid ($K_a = 1.4 \times 10^{-5}$) is represented by the formula HNic. Calculate its per cent dissociation in a solution which contains 0.10 moles of nicotinic acid per 2.0 litre of solution.

Sol.

Ex.4 A solution contains 0.1 M H_2S and 0.3 M HCl. Calculate the conc. of S^{2-} and HS^- ions in solution. Given K_{a_1} and K_{a_2} for H_2S are 10^{-7} and 1.3×10^{-13} respectively.

Sol.

Ex.2 Calculate the conc. of fluoroacetic acid when $[H^+] = 1.50 \times 10^{-3}$ M. K_a of acid = 2.6×10^{-3} .

Sol.

Ex.5 K_1 and K_2 for dissociation of H_2A is 4×10^{-3} and 1×10^{-5} . Calculate A^{2-} concentration in 0.1 M H_2A solution. Also report $[H^+]$ and pH.

Sol.

Ex.3 A saturated solution of o-nitrophenol, has a pH equal to 4.53. What is the solubility of o-nitrophenol in water pK_a for o-nitro-phenol is 7.23.

Sol.

Ex.6 Calculate the pH of a solution which contains 9.9 mL of 1 M HCl and 100 mL of 0.1 M NaOH.

Sol.

Sol.

Ex.7 What will be the resultant pH when 200 mL of an aqueous solution of HCl (pH = 2.0) is mixed with 300 mL of an aqueous solution of NaOH (pH = 12.0) ?

Sol.

Ex.9 What are $[H^+]$, $[A^-]$ and $[B^-]$ in a solution that is 0.03 M HA and 0.1 M HB ? K_a for HA and HB are 1.38×10^{-4} and 1.05×10^{-10} respectively. Also report pH of solution.

Sol.

Ex.10 Calculate the pH of a solution of given mixtures. (a) (2g CH_3COOH + 3g CH_3COONa) in 100 mL of mixture ; $K_a = 1.8 \times 10^{-5}$. (b) 5 mL of 0.1 M NH_4OH + 250 mL of 0.1 M NH_4Cl ; $K_b = 1.8 \times 10^{-5}$ (c) (0.25 mole of acid + 0.35 mole of salt) in 500 mL mixture; $K_a = 3.6 \times 10^{-4}$.

Sol.

Ex.8 A solution contains 0.09 M HCl, 0.09 M $CHCl_2COOH$ and 0.1 M CH_3COOH . The pH of this solution is 1. If K_a for acetic acid is 10^{-5} , calculate K_a for $CHCl_2COOH$.

Ex.11 20 mL of 0.2 M NaOH is added to 50 mL of 0.2 M acetic acid. ($K_a = 1.8 \times 10^{-5}$) (a) What is pH of solution ? (b) Calculate volume of 0.2 M NaOH required to make the pH of solution 4.74.

Sol.

Ex.12 Two buffers (X) and (Y) of pH 4.0 and 6.0 respectively are prepared from acid HA and the salt NaA. Both the buffers are 0.50 M in HA. What would be the pH of the solution obtained by mixing equal volumes of two buffers ? ($K_{HA} = 1.0 \times 10^{-5}$)

Sol.

Ex.13 A certain buffer solution contains equal concentration of X^- and HX. K_b for X^- is 10^{-10} . Calculate pH of buffer.

Sol.

Ex.14 A weak acid HA after treatment with 12 mL of 0.1 M strong base has a pH of 5. At the end point, the volume of same base required is 26.6 mL. Calculate K_a of acid.

Sol.

Ex.15 The $[Ag^+]$ ion in a saturated solution of Ag_2CrO_4 at $25^\circ C$ is 1.5×10^{-4} M. Determine K_{sp} of Ag_2CrO_4 at $25^\circ C$.

Sol.

Ex.16 Will a precipitate of $\text{Mg}(\text{OH})_2$ be formed in a 0.001 M solution of $\text{Mg}(\text{NO}_3)_2$, if the pH of solution is adjusted to 9? K_{sp} of $\text{Mg}(\text{OH})_2 = 8.9 \times 10^{-12}$.

Sol.

Ex.17 Calculate pH of the following mixture. Given that $K_a = 1.8 \times 10^{-5}$ and $K_b = 1.8 \times 10^{-5}$.

- (a) 50 mL of 0.1 M NaOH + 50 mL of 0.05 M CH_3COOH .
- (b) 50 mL of 0.05 M NaOH + 50 mL of 0.10 M CH_3COOH .
- (c) 50 mL of 0.1 M NaOH + 50 mL of 0.10 M CH_3COOH .
- (d) 50 mL of 0.1 M NH_4OH + 50 mL of 0.05 M HCl.
- (e) 50 mL of 0.05 M NH_4OH + 50 mL of 0.1 M HCl.
- (f) 50 mL of 0.10 M NH_4OH + 50 mL of 0.1 M HCl.
- (g) 50 mL of 0.05 M NH_4OH + 50 mL of 0.05 M CH_3COOH .

Sol.

Ex.18 Assuming no change in volume, calculate the minimum mass of NaCl necessary to dissolve 0.010 mole AgCl in 100 litre solution. K_f for $[\text{AgCl}_2]^- = 3 \times 10^5$ and K_{sp} of AgCl = 1.0×10^{-10} .

Sol.

Ex.19 Calculate the concentration of Fe^{2+} in a solution containing 0.2 M $[\text{Fe}(\text{CN})_6]^{4-}$ and 0.10 M CN^- . K_f for $[\text{Fe}(\text{CN})_6]^{4-} = 1 \times 10^{24}$.

Sol.

EXERCISE – I**OBJECTIVE PROBLEMS (JEE MAIN)**

1. The conjugate acid of NH_2^- is

- (A) NH_3 (B) NH_2OH (C) NH_4^+ (D) N_2H_4

Sol.

2. Out of the following, amphiprotic species are

- I : HPO_3^{2-} II OH^- III H_2PO_4^- IV HCO_3^-

- (A) I, III, IV (B) I and III (C) III and IV (D) All

Sol.

3. pH of an aqueous solution of NaCl at 85°C should be

- (A) 7 (B) > 7 (C) < 7 (D) 0

Sol.

4. 1 c.c. of 0.1N HCl is added to 99 CC solution of NaCl. The pH of the resulting solution will be

- (A) 7 (B) 3 (C) 4 (D) 1

Sol.

5. 10 ml of $\frac{M}{200}\text{H}_2\text{SO}_4$ is mixed with 40 ml of

$\frac{M}{200}\text{H}_2\text{SO}_4$. The pH of the resulting solution is

- (A) 1 (B) 2 (C) 2.3 (D) none of these

Sol.

6. If $\text{p}K_b$ for fluoride ion at 25°C is 10.83, the ionisation constant of hydrofluoric acid in water at this temperature is :

- (A) 1.74×10^{-5} (B) 3.52×10^{-3}
(C) 6.75×10^{-4} (D) 5.38×10^{-2}

Sol.

7. The pH of an aqueous solution of 1.0 M solution of a weak monoprotic acid which is 1% ionised is:

- (A) 1 (B) 2 (C) 3 (D) 11

Sol.

8. If K_1 & K_2 be first and second ionisation constant of H_3PO_4 and $K_1 \gg K_2$ which is incorrect.

- (A) $[\text{H}^+] = [\text{H}_2\text{PO}_4^-]$ (B) $[\text{H}^+] = \sqrt{K_1[\text{H}_3\text{PO}_4]}$
(C) $K_2 = [\text{HPO}_4^{2-}]$ (D) $[\text{H}^+] = 3[\text{PO}_4^{3-}]$

Sol.

9. The degree of hydrolysis of a salt of weak acid and weak base in it's 0.1 M solution is found to be 50%. If the molarity of the solution is 0.2 M, the percentage hydrolysis of the salt should be

- (A) 100% (B) 50%
(C) 25% (D) none of these

Sol.

- 10.** What is the percentage hydrolysis of NaCN in $\frac{N}{80}$ solution when the dissociation constant for HCN is 1.3×10^{-9} and $K_w = 1.0 \times 10^{-14}$
- (A) 2.48 (B) 5.26 (C) 8.2 (D) 9.6

Sol.

- 11.** The compound whose 0.1 M solution is basic is
- (A) Ammonium acetate (B) Ammonium chloride
(C) Ammonium sulphate (D) Sodium acetate

Sol.

- 12.** Which of the following solution will have pH close to 1.0 ?

- (A) 100 ml of M/100 HCl + 100 ml of M/10 NaOH
(B) 55 ml of M/10 HCl + 45 ml of M/10 NaOH
(C) 10 ml of M/10 HCl + 90 ml of M/10 NaOH
(D) 75 ml of M/5 HCl + 25 ml of M/5 NaOH

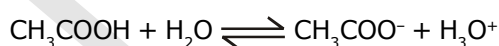
Sol.

- 13.** The \approx pH of the neutralisation point of 0.1 N ammonium hydroxide with 0.1 N HCl is

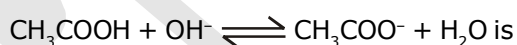
- (A) 1 (B) 6 (C) 7 (D) 9

Sol.

- 14.** If equilibrium constant of



Is 1.8×10^{-5} , equilibrium constant for



- (A) 1.8×10^{-9} (B) 1.8×10^9
(C) 5.55×10^{-9} (D) 5.55×10^{10}

Sol.

- 15.** If 40 ml of 0.2 M KOH is added to 160 ml of 0.1 M HCOOH [$K_a = 2 \times 10^{-4}$]. The pOH of the resulting solution is

- (A) 3.4 (B) 3.7 (C) 7 (D) 10.3

Sol.

16. A solution with pH 2.0 is more acidic than the one with pH 6.0 by a factor of :

- (A) 3 (B) 4
(C) 3000 (D) 10,000

Sol.

17. The first and second dissociation constants of an acid H_2A are 1.0×10^{-5} and 5.0×10^{-10} respectively. The overall dissociation constant of the acid will be:

- (A) 5.0×10^{-5} (B) 5.0×10^{15}
(C) 5.0×10^{-15} (D) 0.2×10^5

Sol.

18. An aqueous solution contains 0.01 M RNH_2 ($K_b = 2 \times 10^{-6}$) & 10^{-4} M NaOH.

The concentration of OH^- is nearly:

- (A) 2.414×10^{-4} M (B) 10^{-4} M
(C) 1.414×10^{-4} M (D) 2×10^{-4} M

Sol.

19. What volume of 0.2 M NH_4Cl solution should be added to 100 ml of 0.1 M NH_4OH solution to produce a buffer solution of pH = 8.7 ?

Given : pK_b of $NH_4OH = 4.7$; $\log 2 = 0.3$

- (A) 50 ml (B) 100 ml
(C) 200 ml (D) none of these

Sol.

Sol.

20. The pK_a of a weak acid, HA, is 4.80. The pK_b of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be:

- (A) 8.58 (B) 4.79
(C) 7.01 (D) 9.22

Sol.

22. How many gm of solid NaOH must be added to 100 ml of a buffer solution which is 0.1 M each w.r.t. Acid HA and salt $Na^+ A^-$ to make the pH of solution 5.5. Given $pK_a(HA) = 5$ (**Use antilog (0.5) = 3.16**)

- (A) 2.08×10^{-1} (B) 3.05×10^{-3}
(C) 2.01×10^{-2} (D) None of these

Sol.

21. The range of most suitable indicator which should be used for titration of $X^- Na^+$ (0.1 M, 10 ml) with 0.1 M HCl should be (Given: $k_{b(X^-)} = 10^{-6}$)

- (A) 2 – 3 (B) 3 – 5 (C) 6 – 8 (D) 8 – 10

23. The solubility of A_2X_3 is $y \text{ mol dm}^{-3}$. Its solubility product is

- (A) $6y^2$ (B) $64 y^4$ (C) $36 y^5$ (D) $108 y^5$

Sol.

24. If K_{sp} for $HgSO_4$ is 6.4×10^{-5} , then solubility of this substance in mole per m^3 is

- (A) 8×10^{-3} (B) 6.4×10^{-5}
(C) 8×10^{-6} (D) None of these

Sol.

25. Which of the following is most soluble in water ?

- (A) MnS ($K_{sp} = 8 \times 10^{-37}$)
(B) ZnS ($K_{sp} = 7 \times 10^{-16}$)
(C) Bi_2S_3 ($K_{sp} = 1 \times 10^{-72}$)
(D) $Ag_3(PO_4)$ ($K_{sp} = 1.8 \times 10^{-18}$)

Sol.

26. 1 M NaCl and 1 M HCl are present in an aqueous solution. The solution is

- (A) not a buffer solution and with $pH < 7$
(B) not a buffer solution with $pH > 7$
(C) a buffer solution with $pH < 7$
(D) a buffer solution with $pH > 7$

Sol.

27. the pK_a of a weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA in which 50% of the acid is ionized is:

- (A) 4.5 (B) 2.5 (C) 9.5 (D) 7.0

Sol.

28. The precipitate of CaF_2 ($K_{sp} = 1.7 \times 10^{-10}$) is obtained when equal volumes of the following are mixed

- (A) $10^{-4} M Ca^{3+} + 10^{-4} M F^-$
(B) $10^{-2} M Ca^{2+} + 10^{-3} M F^-$
(C) $10^{-5} M Ca^{2+} + 10^{-3} M F^-$
(D) $10^{-3} M Ca^{2+} + 10^{-5} M F^-$

Sol.

29. pH of saturated solution of silver salt of monobasic acid HA is found to be 9.

Find the K_{sp} of sparingly soluble salt $Ag A(s)$.

Given : $K_a(HA) = 10^{-10}$

- (A) 1.1×10^{-11} (B) 1.1×10^{-10}
(C) 10^{-12} (D) None of these

Sol.

- (A) $10^{-5}M$ (B) $10^{-6}M$
 (C) $10^{-7}M$ (D) None of these

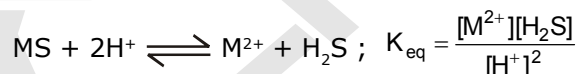
Sol.

30. When equal volumes of the following solutions are mixed, precipitation of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) will occur only with:

- (A) $10^{-4} M$ (Ag^+) and $10^{-4} M$ (Cl^-)
 (B) $10^{-5} M$ (Ag^+) and $10^{-5} M$ (Cl^-)
 (C) $10^{-6} M$ (Ag^+) and $10^{-6} M$ (Cl^-)
 (D) $10^{-10} M$ (Ag^+) and $10^{-10} M$ (Cl^-)

Sol.

32. The solubility of metal sulphides in saturated solution of H_2S ($H_2S = 0.1 M$) can be represented by



The value of K_{eq} is given for few metal sulphide. If conc. of each metal ion in solution is **0.01 M**, which metal sulphides are selectively ppt at total **$[H^+] = 1 M$** in saturated H_2S solution.

Metal sulphides MnS ZnS CoS PbS

$$K_{eq} = \frac{[M^{2+}][H_2S]}{[H^+]^2} \quad 3 \times 10^{10} \quad 3 \times 10^{-2} \quad 3 \quad 3 \times 10^{-7}$$

- (A) MnS, ZnS, CoS (B) PbS, ZnS, CoS
 (C) PbS, ZnS (D) PbS

Sol.

31. 50 litre of a solution containing 10^{-5} mole of Ag^+ is mixed with 50 litre of a $2 \times 10^{-7} M$ HBr solution. $[Ag^+]$ in resultant solution is: [Given : $K_{sp}(AgBr) = 5 \times 10^{-13}$]

33. Solid $Ba(NO_3)_2$ is gradually dissolved in a $1.0 \times 10^{-4} M$ Na_2CO_3 solution. At what concentration of Ba^{2+} will a precipitate begin to form ?
 (K_{sp} for $BaCO_3 = 5.1 \times 10^{-9}$)

- (A) 4.1×10^{-5} M (B) 5.1×10^{-5} M
(C) 8.1×10^{-8} M (D) 8.1×10^{-7} M

Sol.

34. K_{sp} of MX_4 and solubility of MX_4 is S mol/litre is related by:

- (A) $S = [K_{sp}/256]^{1/5}$ (B) $S = [128 K_{sp}]^{1/4}$
(C) $S = [256 K_{sp}]^{1/5}$ (A) $S = [K_{sp}/128]^{1/4}$

Sol.

ASSERTION - REASON

35. Statement-1 : pH of 10^{-7} M NaOH solution is exist between 7 to 7.3 at 25°C .

Statement-2 : Due to common ion effect ionization of water is reduced.

- (A) Statement (1) is correct and statement (2) is correct and statement (2) is correct explanation for (1)
(B) Statement (1) is correct and statement (2) is correct and statement (2) is NOT correct explanation for (1)
(C) Statement (1) is true but (2) is false
(D) Statement (1) is false but (2) is true

Sol.

36. Statement-1 : In general phenolphthalein is used as an indicator for the titration of weak acid (HA) against strong base (NaOH).

Statement-2 : At equivalent point solution is basic.

- (A) Statement (1) is correct and statement (2) is correct and statement (2) is correct explanation for (1)
(B) Statement (1) is correct and statement (2) is correct and statement (2) is NOT correct explanation for (1)
(C) Statement (1) is true but (2) is false
(D) Statement (1) is false but (2) is true

Sol.

37. Statement-1 : Moles of Sr^{2+} of furnished by sparingly soluble substance $\text{Sr}(\text{OH})_2$ decreases due to dilution in its saturated solution.

Statement-2 : Solubility product constant of $\text{Sr}(\text{OH})_2$ is not affected by dilution.

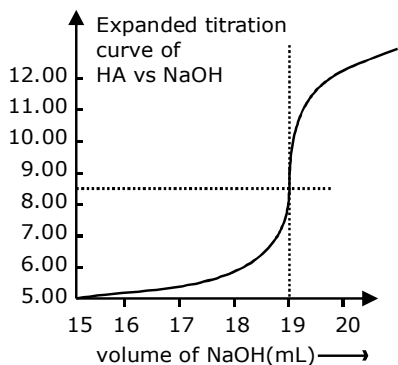
- (A) Statement (1) is correct and statement (2) is correct and statement (2) is correct explanation for (1)
(B) Statement (1) is correct and statement (2) is correct and statement (2) is NOT correct explanation for (1)
(C) Statement (1) is true but (2) is false
(D) Statement (1) is false but (2) is true

Sol.

Comprehension

Paragraph for Question 38 to 40

1.2 of a monoprotic acid HA, is titrated with 0.222 M NaOH solution. The pH of the solution is monitored with pH meter. A portion of the titration curve is shown in the diagram.



38. How many mL of NaOH is required to bring about the titration to its equivalence point?

- (A) 4.00 (B) 9.00
(C) 19.00 (D) None of these

Sol.

39. What is the pH of solution at the equivalence point?

- (A) 3.50 (B) 7.00
(C) 8.40 (D) 5

Sol.

40. What is the molar mass of HA?

- (A) 180 (B) 222
(C) 282 (D) None of these

Sol.

Paragraph for Quesiton 41 to 44

Potash alum is $\text{K Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. As a strong eletrolyte, it is considered to be 100% dissociated into K^+ , Al^{3+} and SO_4^{2-} . The solution is acidic because of the hydrolysis of Al^{3+} , but not so acidic as might be expected, because the SO_4^{2-} can sponge up some the H_3O^+ by forming HSO_4^- . Given a solution made by dissolving 11.85 gm of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ in enough water to make 100 cm^3 of solution. What is $[\text{H}_3\text{O}^+]$ of the solution if

41. None of the ion is hydrolysing

- (A) 10^{-7}M (B) less than 10^{-7}M
(C) More than 10^{-7}M (D) 0.0

Sol.

42. Only Al^{3+} is hydrolysing and its first hydrolysis constant is 1.4×10^{-5} M

- (A) 1.87×10^{-3} M (B) 6.24×10^{-4} M
(C) 0.09 M (D) None of these

Sol.

43. Only SO_4^{2-} is hydrolysing and acid dissociation constant of HSO_4^- in water is 1.25×10^{-2} .

- (A) 1.26×10^{-3} M (B) 6.32×10^{-7} M
(C) 1.58×10^{-8} M (D) None of these

Sol.

44. Both Al^{3+} and SO_4^{2-} are hydrolysing.

- (A) 2.93×10^{-4} M (B) 0.0114 M
(C) 5.43×10^{-6} M (D) None of these

Sol.

Match The column

45. Column-I

(A) $\left(\begin{array}{l} 10 \text{ litre of } 0.03 \text{ N } \text{X}(\text{OH})_2 \text{ (strong diacidic base)} \\ + \\ 5 \text{ litre of } 0.08 \text{ M } \text{HNO}_3 \\ + \\ 485 \text{ litre of } 0.01 \text{ M } \text{NaNO}_3 \end{array} \right)$

(B) $\left(\begin{array}{l} 10 \text{ ml of } 0.5 \text{ M } \text{RNH}_3\text{Cl} (\text{K}_h = 10^{-9}) \\ + \\ 40 \text{ ml of } 0.125 \text{ M } \text{KOH} \end{array} \right)$

(C) $\left(\begin{array}{l} 100 \text{ ml of } 0.8 \text{ M } \text{HCO}_3^- \\ + \\ 100 \text{ ml of } 0.4 \text{ M } \text{CO}_3^{2-} \\ \left(\text{for } \text{H}_2\text{CO}_3, \text{ use } \text{K}_{a_1} = 4 \times 10^{-7} \text{ \& } \text{K}_{a_2} = 4 \times 10^{-11} \right) \end{array} \right)$

(D) Saturated aqueous solution of $\text{Co}(\text{OH})_3$ ($\text{K}_{sp} = 2.7 \times 10^{-43}$)

Column-II

(P) $\text{pH} \approx 3.7$

(Q) $\text{pH} \approx 11$

(R) $\text{pH} \approx 7$

(S) $\text{pH} \approx 10$

Sol.

46. Column-I (pH of the resultant solution)

(A) 200 ml of H_2SO_4 solution (specific gravity 1.225 containing 25% H_2SO_4 by weight) + 800 ml of 0.525 M strong triacidic base $\text{X}(\text{OH})_3$

(B) 50 ml of 0.1 M HCO_3^- + 50 ml of 0.8 M CO_3^{2-} ($\text{H}_2\text{CO}_3: \text{K}_{a_1} = 4 \times 10^{-7}, \text{K}_{a_2} = 2 \times 10^{-11}$)

(C) 50 ml of 0.2 M $\text{HA}(\text{aq})$ ($\text{K}_a = 10^{-5}$) + 50 ml of 0.1 M $\text{HCl}(\text{aq})$ + 100 ml of 0.13 M $\text{NaOH}(\text{aq})$

Column-II (Exist b/w colour transition range of an indicator)

(P) Phenol Red (6.8 to 8.4)

(Q) Propyl red (4.6 to 6.4)

(R) Phenolphthalein (8.3 to 10.1)

(S) Malachite green (11.4 to 13)

Sol.

Sol.

- 47.** Find the pH of solution prepared by mixing 25ml of a 0.5 M solution of HCl, 10ml of a 0.5 M solution of NaOH and 15ml of water –
- (A) 0.8239 (B) 1.0029
(C) 1.0239 (D) 1.8239

Sol.

- 49.** Determine degree of dissociation of 0.05 M NH_3 at 25°C in a solution of pH = 11.
- (A) 2% (B) 4%
(C) 5% (D) 10%

Sol.

- 50.** Ostwald's dilution law gives satisfactory results for –
- (A) HCl (B) HNO_3
(C) CH_3COOH (D) NaOH

Sol.

- 48.** Which of the following has pH is equal to near about one –
- (A) 100 ml $\frac{M}{10}$ HCl + 100ml $\frac{M}{10}$ NaOH
(B) 55 ml $\frac{M}{10}$ HCl + 44 ml $\frac{M}{10}$ NaOH
(C) 10 ml $\frac{M}{10}$ HCl + 90 ml $\frac{M}{10}$ NaOH
(5) 75 ml $\frac{M}{5}$ HCl + 25ml $\frac{M}{5}$ NaOH

EXERCISE – II**OBJECTIVE PROBLEMS (JEE ADVANCED)**

1. Which of the following statement(s) is/are correct?
 (A) the pH of 1.0×10^{-8} M solution of HCl is 8
 (B) the conjugate base of H_2PO_4^- is HPO_4^{2-}
 (C) autoprotolysis constant of water increases with temperature
 (D) When a solution of a weak monoprotic acid is titrated again a strong base, at half-neutralization point $\text{pH} = (1/2) \text{pK}_a$.

Sol.

2. A 2.5 gm impure sample containing weak monoacidic base (Mol. wt. = 45) is dissolved in 100 ml water and

titrated with 0.5 M HCl when $\left(\frac{1}{5}\right)^{\text{th}}$ of the base was

neutralised the pH was found to be 9 and at equivalent point pH of solution is 4.5. Given : All data at 25°C & $\log 2 = 0.3$.

Select **correct** statement(s).

- (A) K_b of base is less than 10^{-6}
 (B) Concentration of salt (C) at equivalent point is 0.25 M
 (C) Volume of HCl is used at equivalent point is 100 ml
 (D) Weight percentage of base in given sample is 80%

Sol.

3. Select **incorrect** statement(s).

- (A) Phenolphthalein is suitable indicator for the titration of $\text{HCl}(\text{aq})$ with $\text{NH}_4\text{OH}(\text{aq})$.
 (B) An acid-base indicator in a buffer solution of $\text{pH} = \text{pK}_{\text{in}} + 1$ is ionized to the extent of 90%
 (C) In the titration of a monoacidic weak base with a strong acid, the pH at equivalent point is always

calculated by $\text{pH} = \frac{1}{2} [\text{pK}_w - \text{pK}_b - \log C]$

- (D) When $\text{Na}_3\text{PO}_4(\text{aq})$ is titrated with $\text{HCl}(\text{aq.})$, the pH of solution at second equivalent point is calculated

by $\frac{1}{2} [\text{pK}_{a_1} + \text{pK}_{a_2}]$

Sol.

4. Which of the following is true for alkaline aqueous solution?

- (A) $\text{pH} > \frac{\text{pK}_w}{2}$ (B) $\text{pH} > \text{pOH}$ (C) $\text{pOH} < \frac{\text{pK}_w}{2}$ (D) $\text{pH} < \text{pOH}$

Sol.

5. A buffer solution can be prepared from a mixture of

- (A) sodium acetate and acetic acid in water
 (B) sodium acetate and hydrochloric acid in water
 (C) ammonia and ammonium chloride in water
 (D) ammonia and sodium hydroxide in water.

Sol.

6. A solution contains HCl, $\text{Cl}_2\text{HC COOH}$ & CH_3COOH at concentration 0.09 M in HCl, 0.09 M in $\text{Cl}_2\text{HC COOH}$ & 0.1 M in CH_3COOH . pH for the solution is 1. Ionization constant of $\text{CH}_3\text{COOH} = 10^{-5}$. What is the magnitude of K for dichloroacetic acid ?

- (A) $K_a = 1.25 \times 10^{-2}$ (B) $K_a = 2.25 \times 10^{-2}$
 (C) $K_a = 3.75 \times 10^{-4}$ (D) $K_a = 5.75 \times 10^{-2}$

Sol.

7. A solution of chloroacetic acid, ClCH_2COOH containing 9.45 grams in 500 ml of the solution has a pH of 2.0. What is the degree of ionization the acid.

- (A) $\alpha = 0.09$ (B) $\alpha = 0.05$
(C) $\alpha = 0.07$ (D) $\alpha = 0.15$

Sol.

8. The K_w of water at two different temperature is :

T 25°C 50°C

K_w 1.08×10^{-14} 5.474×10^{-14}

Assuming that ΔH of any reaction is independent of temperature, calculate the enthalpy of neutralization of strong acid and strong base.

- (A) $\Delta H_{\text{neut}} = -59.963 \text{ kJ mol}^{-1}$
(B) $\Delta H_{\text{neut}} = -67.967 \text{ kJ mol}^{-1}$
(C) $\Delta H_{\text{neut}} = -62.693 \text{ kJ mol}^{-1}$
(D) $\Delta H_{\text{neut}} = -51.963 \text{ kJ mol}^{-1}$

Sol.

9. The equilibrium constant of the reaction.



is 1.2×10^{-23} at 25°C. Calculate the pH of a solution at equilibrium with the iodine ion concentration = 0.10 and the pressure of H_2 gas = 0.60 atm.

- (A) 3.560 (B) 6.660 (C) 1.650 (D) 5.650

Sol.

10. When a 40 mL of a 0.1 M weak base is titrated with 0.16 M HCl, the pH of the solution at the end point is 5.23. What will be the pH if 15 mL of 0.12 M NaOH is added to the resulting solution.

- (A) 2.861 (B) 9.168 (C) 7.168 (D) 5.816

Sol.

11. How many moles of sodium hydroxide can be added to 1.00 L of a solution 0.1 M in NH_3 & 0.1 M in NH_4Cl without changing the pOH by more than 1.00 unit? Assume no change in volume. $K_b(\text{NH}_3) = 1.8 \times 10^{-5}$.

- (A) 0.0818 moles (B) 0.0516 moles
(C) 0.0718 moles (D) 0.0926 moles

Sol.

12. 20 ml of a solution of 0.1 M CH_3COOH solution is being titrated against 0.1 M NaOH solution. The pH values after the addition of 1 ml & 19 ml of NaOH are $(\text{pH})_1$ & $(\text{pH})_2$, what is ΔpH ?

- (A) 4.858 (B) 8.588
(C) 3.858 (D) 2.558

Sol.

13. Calculate the OH^- concentration and the H_3PO_4 concentration of a solution prepared by dissolving 0.1 mol of Na_3PO_4 in sufficient water to make 1 l of solution. $K_1 = 7.1 \times 10^{-3}$, $K_2 = 6.3 \times 10^{-8}$, $K_3 = 4.5 \times 10^{-13}$.

- (A) $[\text{OH}^-] = 3.73 \times 10^{-18} \text{ M}$, $[\text{H}_3\text{PO}_4] = 6 \times 10^{-3} \text{ M}$
(B) $[\text{OH}^-] = 3.73 \times 10^{-4} \text{ M}$, $[\text{H}_3\text{PO}_4] = 6 \times 10^{-22} \text{ M}$
(C) $[\text{OH}^-] = 3.73 \times 10^{-2} \text{ M}$, $[\text{H}_3\text{PO}_4] = 6 \times 10^{-18} \text{ M}$
(D) $[\text{OH}^-] = 3.73 \times 10^{-4} \text{ M}$, $[\text{H}_3\text{PO}_4] = 6 \times 10^{-16} \text{ M}$

Sol.

14. Solubility product of AgCl is 2.8×10^{-10} at 25°C . Calculate solubility of the salt in 0.1 M AgNO_3 solution-

- (A) 2.8×10^{-9} mole/litre (B) 2.8×10^{-10} mole/litre
(C) 3.2×10^{-9} mole/litre (D) 3.2×10^{-12} mole/litre

Sol.

15. Equilibrium constant for the acid ionization of Fe^{3+} to $\text{Fe}(\text{OH})^{+2}$ and H^+ is 6.5×10^{-3} . What is the max. pH, which could be used so that at least 95% of the total Fe^{3+} in a dilute solution, exists as Fe^{3+} .

- (A) 0.608 (B) 2.908 (C) 1.508 (D) 0.908

Sol.

16. A solution of weak acid HA was titrated with base NaOH. The equivalence point was reached when 36.12 ml of 0.1 M NaOH has been added. Now 18.06 ml of 0.1 M HCl were added to titration solution, the pH was found to be 4.92. What will be the pH of the solution obtained by mixing 10 ml 0.2 M NaOH and 10 ml of 0.2 M HA .

- (A) 10.96 (B) 8.96 (C) 12.96 (D) 6.96

Sol.

17. A weak base BOH was titrated against a strong acid. The pH at $1/4$ the equivalence point was 9.24. Enough strong base was now added (6m eq.) to completely convert the salt. The total volume was 50 ml. Find the pH at this point.

- (A) 11.22 (B) 22.44 (C) 33.44 (D) 44.88

Sol.

18. At 25°C , will a precipitate of $\text{Mg}(\text{OH})_2$ form in a 10^{-4} M solution of $\text{Mg}(\text{NO}_3)_2$ if pH of the solution is adjusted to 9.0. $K_{sp} [\text{Mg}(\text{OH})_2] = 10^{-11} \text{ M}^3$. At what min value of pH will precipitation start.

- (A) 9 (B) 18 (C) 27 (D) 6

Sol.

19. What is the solubility of AgCl in 0.20 M NH_3 ?

Given : $K_{sp}(\text{AgCl}) = 1.7 \times 10^{-10} \text{ M}^2$, $K_1 = [\text{Ag}(\text{NH}_3)^+] / [\text{Ag}^+][\text{NH}_3] = 2.33 \times 10^3 \text{ M}^{-1}$ and

$K_2 = [\text{Ag}(\text{NH}_3)_2^+] / [\text{Ag}(\text{NH}_3)^+][\text{NH}_3] = 7.14 \times 10^3 \text{ M}^{-1}$

- (A) 6.66×10^{-3} (B) 9.66×10^{-5}
(C) 9.66×10^{-3} (D) 6.66×10^{-5}

Sol.

20. Equal volumes of 0.02 M AgNO_3 and 0.02 M HCN were mixed. Calculate $[\text{Ag}^+]$ at equilibrium. Take $K_a(\text{HCN}) = 9 \times 10^{-10}$, $K_{sp}(\text{AgCN}) = 4 \times 10^{-6}$.

- (A) $[\text{Ag}^+] = 5.699 \times 10^{-5} \text{ M}$ (B) $[\text{Ag}^+] = 6.669 \times 10^{-5} \text{ M}$
(C) $[\text{Ag}^+] = 11.66 \times 10^{-5} \text{ M}$ (D) $[\text{Ag}^+] = 12.669 \times 10^{-5} \text{ M}$

Sol.

EXERCISE – III**SUBJECTIVE PROBLEMS (JEE ADVANCED)**

1. Calculate change in concentration of H^+ ion in one litre of water, when temperature changes from 298 K to 310 K. Given $K_w(298) = 10^{-14}$ $K_w(310) = 2.56 \times 10^{-14}$

Sol.

2. Calculate the number of H^+ present in one ml of solution whose pH is 13.

Sol.

3. pH of dilute solution of HCl is 6.95. Calculate molarity of HCl solution

Sol.

4. Calculate pH of following solutions :

- (a) 0.1 M HCl (b) 0.1 M CH_3COOH ($K_a = 1.8 \times 10^{-5}$)
(c) 0.1 M NH_4OH ($K_a = 1.8 \times 10^{-5}$)
(d) 0.1 M H_2SO_4 (50 ml) + 0.4 M HCl (50 ml)
(e) 10^{-8} M HCl (f) 10^{-10} M NaOH
(g) Decimolar solution of Baryta ($Ba(OH)_2$), diluted 100 times
(h) 10^{-3} mole of KOH dissolved in 100 L of water.
(i) 0.5 M HCl (25 ml) + 0.5 M NaOH (10 ml) + 40 ml H_2O
(j) Equal volume of HCl solution (PH = 4) + 0.0019 N HCl solution
(k) 10^{-6} M CH_3COOH ($K_a = 1.8 \times 10^{-5}$)
(l) 10^{-8} M CH_3COOH ($K_a = 1.8 \times 10^{-5}$)

Sol.

5. Calculate :

- (a) K_a for monobasic acid and whose 0.10 M solution has pH of 4.50
(b) K_b for a monoacidic base whose 0.10 M solution has a pH of 10.50.

Sol.

6. Calculate the ratio of degree of dissociation $\left(\frac{\alpha_2}{\alpha_1}\right)$ when 1 M acetic acid solution is diluted to 1/100 times.
[Given $K_a = 10^{-5} \text{M}$]

Sol.

7. Calculate the ratio of degree of dissociation of acetic acid and hydrocyanic acid (HCN) in 1 M their respective solution of acids.

[Given $K_{a(\text{CH}_3\text{COOH})} = 1.8 \times 10^{-5}$; $K_{a(\text{HCN})} = 6.2 \times 10^{-10}$]

Sol.

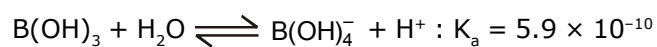
8. The pH of aqueous solution of ammonia is 11.5. Find molarity of solution. $K_b (\text{NH}_4\text{OH}) = 1.8 \times 10^{-5}$.

Sol.

9. The solution of weak monoprotic acid which is 0.01 M has pH = 3. Calculate K_a of weak acid.

Sol.

10. Boric acid is a weak monobasic acid. It ionizes in water as



Calculate pH of 0.3 M boric acid.

Sol.**Sol.**

11. Calculate $[H^+]$ and $[CHCl_2COO^-]$ in a solution that is 0.01 M in HCl and 0.01 M in $CHCl_2COOH$.

Take ($K_a = 2.55 \times 10^{-2}$).

Sol.

13. Calculate pH of resultant solution of 0.1 M HA + 0.1 M HB

$[K_a(HA) = 2 \times 10^{-5}; K_a(HB) = 4 \times 10^{-5}]$

Sol.

12. Calculate $[H^+]$, $[CH_3COO^-]$ and $[C_7H_5O_2^-]$ in solution that is 0.02 M in acetic acid and 0.01 M in benzoic acid. K_a (acetic) = 1.8×10^{-5} , K_a (benzoic) = 6.4×10^{-5} .

POLYPROTIC ACIDS & BASES

14. Calculate $[H^+]$, $[H_2PO_4^-]$, $[HPO_4^{2-}]$ and $[PO_4^{3-}]$ in a 0.01 M solution of H_3PO_4 .

Take $K_1 = 10^{-3}$, $K_2 = 10^{-8}$, $K_3 = 10^{-13}$.

Sol.

15. Calculate the pH of 0.1 M solution of $H_2NCH_2CH_2NH_2$; ethylenediamine (en). Determine the en H_2^{2+} concentration in the solution. K_{b1} and K_{b2} values of ethylenediamine are 8.5×10^{-5} and 7.1×10^{-8} respectively.

Sol.

16. What are the concentrations of H^+ , HSO_4^- , SO_4^{2-} and H_2SO_4 in a 0.20 M solution of sulphuric acid?

Given : $H_2SO_4 \rightarrow H^+ + HSO_4^-$; strong

$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$; $K_2 = 10^{-2}$ M

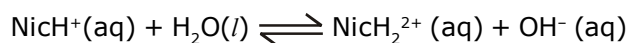
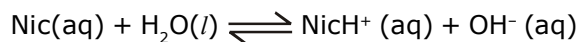
Sol.

17. What are the concentrations of H^+ , $H_2C_2O_4$, $HC_2O_4^-$ and $C_2O_4^{2-}$ in a 0.1 M solution of oxalic acid?

$[K_1 = 10^{-2}$ M and $K_2 = 10^{-5}$ M]

Sol.

18. Nicotine, $C_{10}H_{14}N_2$, has two basic nitrogen atoms and both can react with water to give a basic solution



K_{b1} is 7×10^{-7} and K_{b2} is 10^{-10} . Calculate the approximate pH of 0.020 M solution.

Sol.

19. H_3A is a weak triprotic acid ($K_{a1} = 10^{-5}$, $K_{a2} = 10^{-9}$, $K_{a3} = 10^{-13}$)

Calculate the value of pX of 0.1 M $H_3A(\text{aq})$ solution

where $\text{pX} = -\log X$ & $X = \frac{[A^{3-}]}{[HA^{2-}]}$.

Sol.

BUFFER SOLUTION

20. Determine $[\text{OH}^-]$ of 0.050 M solution of ammonia to which sufficient NH_4Cl has been added to make the total $[\text{NH}_4^+]$ equal to 0.100. [$K_{b(\text{NH}_3)} = 1.8 \times 10^{-5}$]

Sol.

21. Calculate the pH of solution prepared by mixing 50.0 mL of 0.200 M $\text{HC}_2\text{H}_3\text{O}_2$ and 50.0 mL of 0.100 M NaOH. [$K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$]

Sol.

22. A buffer of pH 9.26 is made by dissolving x moles of ammonium sulphate and 0.1 mole of ammonia into 100 mL solution. If pK_b of ammonia is 4.74, calculate value of x .

Sol.

23. 50 mL of 0.1 M NaOH is added to 75 mL of 0.1 M NH_4Cl to make a basic buffer. If pK_a of NH_4^+ is 9.26, calculate pH.

Sol.

24. (a) Determine the pH of a 0.2 M solution of pyridine C_5H_5N . $K_b = 1.5 \times 10^{-9}$

Sol.

(b) Predict the effect of addition of pyridinium ion $C_5H_5NH^+$ on the position of the equilibrium. Will the pH be raised or lowered ?

Sol.

(c) Calculate the pH of 1.0 L of 0.10 M pyridine solution to which 0.3 mol of pyridinium chloride $C_5H_5NH^+Cl$, has been added, assuming no change in volume.

Sol.

25. Calculate the pH of a solution which results from the mixing of 50.0 ml of 0.3 M HCl with 50.0 ml of 0.4 M NH_3 . [$K_b(NH_3) = 1.8 \times 10^{-5}$]

Sol.

26. Calculate the pH of a solution made by mixing 50.0 ml of 0.2 M NH_4Cl & 75.0 ml of 0.1 M NaOH [$K_b(NH_3) = 1.8 \times 10^{-5}$]

Sol.

INDICATORS

27. For the acid indicator thymol blue, pH is 2.0 when half the indicator is in unionised form. Find the % of indicator in unionised form in the solution with $[H^+] = 4 \times 10^{-3}$ M.

Sol.

28. At what pH does an indicator change colour if the indicator is a weak acid with $K_{\text{ind}} = 4 \times 10^{-4}$. For which one(s) of the following neutralizations would the indicator be useful ? Explain.

(a) $\text{NaOH} + \text{CH}_3\text{COOH}$ (b) $\text{HCl} + \text{NH}_3$ (c) $\text{HCl} + \text{NaOH}$

Sol.

Sol.

29. What indicator should be used for the titration of 0.10 M KH_2BO_3 with 0.10 M HCl ?

$$K_a(\text{H}_3\text{BO}_3) = 7.2 \times 10^{-10}$$

Sol.

31. An acid base indicator has a K_a of 3×10^{-5} . The acid form of the indicator is red & the basic form is blue. By how much must the pH change in order to change the indicator from 75% red to 75% blue ?

Sol.

30. Bromophenol blue is an acid indicator with a K_a value of 6×10^{-5} . What % of this indicator is in its basic form at a pH of 5 ?

HYDROLYSIS

32. What is the OH^- concentration of a 0.08 M solution of CH_3COONa . [$K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$]

Sol.

33. Calculate the pH of a 2.0 M solution of NH_4Cl . [$K_b(\text{NH}_3) = 1.8 \times 10^{-5}$]

Sol.

34. 0.25 M solution of pyridinium chloride $\text{C}_5\text{H}_6\text{N}^+ \text{Cl}^-$ was found to have a pH of 2.699. What is K_b for pyridine, $\text{C}_5\text{H}_5\text{N}$?

Sol.

35. Calculate the extent of hydrolysis & the pH of 0.02 M $\text{CH}_3\text{COONH}_4$.

[$K_b(\text{NH}_3) = 1.8 \times 10^{-5}$, $K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$]

Sol.

36. Calculate the percent hydrolysis in a 0.06 M solution of KCN. [$K_a(\text{HCN}) = 6 \times 10^{-10}$]

Sol.

37. Calculate the extent of hydrolysis of 0.005 M K_2CrO_4 . [$K_2 = 3.1 \times 10^{-7}$ for H_2CrO_4]

(It is essentially strong for first ionization)

Sol.

38. Calculate the percent hydrolysis in a 0.0100 M solution of KCN. ($K_a = 6.2 \times 10^{-10}$)

Sol.

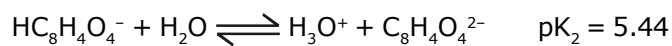
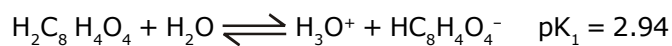
39. A 0.010 M solution of $\text{PuO}_2(\text{NO}_3)_2$ was found to have a pH of 4.0. What is the hydrolysis constant, K_h , for PuO_2^{2+} , and what is K_b for $\text{PuO}_2 \text{OH}^+$?

Sol.

40. Calculate the pH of 1.0×10^{-3} M sodium phenolate, NaOC_6H_5 . for HOC_6H_5 is 1.05×10^{-10}

Sol.

42. Calculate pH of 0.05 M potassium hydrogen phthalate, $\text{KHC}_8\text{H}_4\text{O}_4$.



Sol.

43. The acid ionization (hydrolysis) constant of Zn^{2+} is 1.0×10^{-9}

(a) Calculate the pH of a 0.001 M solution of ZnCl_2

(b) What is the basic dissociation constant of Zn(OH)^+ ?

Sol.

41. What is the pH of 0.1 M NaHCO_3 ? $K_1 = 4.5 \times 10^{-7}$, $K_2 = 4.5 \times 10^{-11}$ for carbonic acids.

Sol.

ACID BASE REACTIONS & TITRATIONS

44. Calculate OH^- concentration at the equivalent point when a solution of 0.1 M acetic acid is titrated with a solution of 0.1 M NaOH. K_a for the acid = 1.9×10^{-5} .

Sol.

45. Calculate the hydronium ion concentration and pH at the equivalence point in the reaction of 22.0 mL of 0.10 M acetic acid, CH_3COOH , with 22.0 mL of 0.10 M NaOH. ($K_a = 1.8 \times 10^{-5}$)

Sol.

46. Calculate the hydronium ion concentration and the pH at the equivalence point in a titration of 50.0 mL of 0.40 M NH_3 with 0.40 M HCl. ($K_b = 1.8 \times 10^{-5}$)

Sol.

47. In the titration of a solution of a weak acid HX with NaOH, the pH is 5.8 after 10.0 mL of NaOH solution has been added and 6.402 after 20.0 mL of NaOH has been added. What is the ionization constant of HX ?

Sol.

48. The equivalent point in a titration of 40.0 mL of a solution of weak monoprotic acid occurs when 35.0 mL of a 0.10 M NaOH solution has been added. The pH of the solution is 5.75 after the addition of 20.0 mL of NaOH solution. What is the dissociation constant of the acid ?

Sol.

49. A weak base (50.0 mL) was titrated with 0.1 M HCl. The pH of the solution after the addition of 10.0 mL and 25.0 mL were found to be 9.84 and 9.24, respectively. Calculate K_b of the base and pH at the equivalence point.

Sol.

50. A weak acid (50.0 mL) was titrated with 0.1 M NaOH. The pH values when 10.0 mL and 25.0 mL of base have been added are found to be 4.16 and 4.76, respectively. Calculate K_a of the acid and pH the equivalence point.

Sol.

51. CH_3COOH (50 ml, 0.1 M) is titrated against 0.1 M NaOH solution. Calculate the pH at the addition of 0 ml, 10 ml, 20 ml, 25 ml, 40 ml, 50 ml of NaOH. K_a of CH_3COOH is 2×10^{-5} .

Sol.

SOLUBILITY & SOLUBILITY PRODUCTS

52. The values of K_{sp} for the slightly soluble salts MX and QX_2 are each equal to 4.0×10^{-18} . Which salt is more soluble ? Explain your answer fully.

Sol.

53. The solubility of $PbSO_4$ in water is 0.038 g/L. Calculate the solubility product constant of $PbSO_4$ in water.

Sol.

54. How many mol CuI ($K_{sp} = 5 \times 10^{-12}$) will dissolve in 1.0 L of 0.10 M NaI solution ?

Sol.

55. A solution of saturated CaF_2 is found to contain 4.1×10^{-4} M fluoride ion. Calculate the K_{sp} of CaF_2 . Neglect hydrolysis.

Sol.

56. The solubility of ML_2 (formula weight, 60 g/mol) in water is 2.4×10^{-5} g/100 mL solution. Calculate solubility product constant for ML_2 .

Sol.

57. What is the solubility (in mol/L) of $Fe(OH)_3$ in a solution of $pH = 8.0$? [K_{sp} for $Fe(OH)_3 = 1.0 \times 10^{-36}$]

Sol.

58. Calculate the solubility of A_2X_3 in pure water, assuming that neither kind of ion reacts with water. For A_2X_3 , $[K_{sp} = 1.1 \times 10^{-23}]$

Sol.

59. Determine the solubility of AgCl in 0.1 M $BaCl_2$. $[K_{sp} \text{ for AgCl} = 1 \times 10^{-10}]$

Sol.

60. What mass of Pb^{2+} ion is left in solution when 50.0 mL of 0.20 M $Pb(NO_3)_2$ is added to 50.0 ml 1.5 M NaCl

[Given K_{sp} for $PbCl_2 = 1.7 \times 10^{-4}$]

Sol.

61. A solution has a Mg^{2+} concentration of 0.0010 mol/L. Will $Mg(OH)_2$ precipitate if the OH^- concentration of the solution is $[K_{sp} = 1.2 \times 10^{-11}]$

(a) 10^{-5} mol/L (b) 10^{-3} mol/L ?

Sol.

62. Calculate solubility of PbI_2 ($K_{sp} = 1.4 \times 10^{-8}$) in water at 25° , which is 90% dissociated

Sol.

63. 500 mL of 0.01 $AgNO_3$ is mixed with 250 ml each of NaBr and NaCl, each having molarity 0.02 M. Find equilibrium concentration of Br^- (moles/L).

Given : $K_{sp}(AgBr) = 5 \times 10^{-13}$, $K_{sp}(AgCl) = 10^{-10}$.

Sol.

64. Calculate solubility of AgCN ($K_{sp} = 4 \times 10^{-16}$) in a buffer solution of PH = 3. [$(K_a)_{HCl} = 4 \times 10^{-10}$]

Sol.

SIMULTANEOUS SOLUBILITY

65. Calculate the Simulataneous solubility of AgSCN and AgBr. $K_{sp}(\text{AgSCN}) = 1.1 \times 10^{-12}$, $K_{sp}(\text{AgBr}) = 5 \times 10^{-13}$.

Sol.

66. Calculate F^- in a solution saturated with respect of both MgF_2 and SrF_2 . $K_{sp}(MgF_2) = 9.5 \times 10^{-9}$, $K_{sp}(SrF_2) = 4 \times 10^{-9}$.

Sol.

COMPLEXATION EQUILIBRIA

67. Assuming no change in volume, calculate the minimum mass of NaCl necessary to dissolve 0.010 mol AgCl in 100 L solution :

[$K_1(\text{AgCl}_2^-) = 3 \times 10^5$, $K_{sp}(\text{AgCl}) = 1 \times 10^{-10}$]

Sol.

68. A recent investigation of the complexation of SCN^- with Fe^{3+} represented by constant K_1 , K_2 and K_3 as 130, 16, and 1.0 respectively. What is the overall formation constant of $Fe(SCN)_3$ from its component ions, and what is the dissociation constant of $Fe(SCN)_3$ into its simplest ions on the basis of these data ?

Sol.

69. How much AgBr could dissolve in 1.0 L of 0.40 M NH_3 ? Assume that $\text{Ag}(\text{NH}_3)_2^+$ is the only complex formed.

$$[K_f(\text{Ag}(\text{NH}_3)_2^+) = 1 \times 10^8 ; K_{sp}(\text{AgBr}) = 5 \times 10^{-13}]$$

Sol.

Sol.

72. A handbook states that the solubility of methylamine $\text{CH}_3\text{NH}_2(\text{g})$ in water at 1 atm pressure at 25°C is 959 volumes of $\text{CH}_3\text{NH}_2(\text{g})$ per volume of water ($\text{p}K_b = 3.39$)

(a) Estimate the max. pH that can be attained by dissolving methylamine in water.

(b) What molarity NaOH (aq.) would be required to yield the same pH ?

Sol.

Miscellaneous

70. Calculate the percent error in the $[\text{H}_3\text{O}^+]$ concentration made by neglecting the ionization of water in 10^{-6} M NaOH solution.

Sol.

73. Mixture of solutions. Calculate the pH of the following solutions. $K_1 = 7.5 \times 10^{-3}\text{ M}$;

$$K_2 = 6.2 \times 10^{-8}\text{ M} ; K_3 = 1.0 \times 10^{-12}\text{ M}$$

(A) 50 ml of $0.12\text{ M H}_3\text{PO}_4$ + 20 ml of 0.15 M NaOH ;

(B) 50 ml of $0.12\text{ M H}_3\text{PO}_4$ + 40 ml of 0.15 M NaOH ;

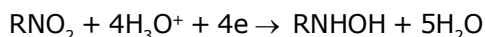
(C) 40 ml of $0.12\text{ M H}_3\text{PO}_4$ + 40 ml of 0.18 M NaOH ;

(D) 40 ml of $0.10\text{ M H}_3\text{PO}_4$ + 40 ml of 0.25 M NaOH .

Sol.

71. What is the pH of 1.0 M solution of acetic acid? To what volume must 1 litre of the solution be dilute so that the pH of the resulting solution will be twice the original value. Given $K_a = 1.8 \times 10^{-5}$.

74. The electrolytic reduction of an organic nitro compound was carried out in a solution buffered by acetic acid and sodium acetate. The reaction was



300 ml of 0.0100 M solution of RNO_2 buffered initially at pH 5.00 was reduced, with the reaction above going to completion. The total acetate concentration, $[\text{HOAc}] + [\text{OAc}^-]$, was 0.50 M. Calculate the pH of the solution after the reduction is complete.

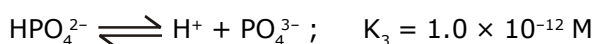
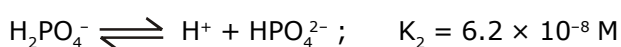
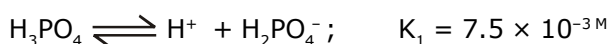
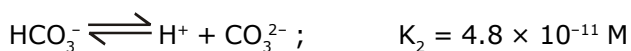
$$(\text{K}_a)_{\text{CH}_3\text{COOH}} = 1.8 \times 10^{-5}$$

Sol.

75. It is desired to prepare 100 ml of a buffer of pH 5.00. Acetic, benzoic and formic acids and their salt are available for use. Which acid should be used for maximum effectiveness against increase in pH? What acid-salt ratio should be used? pK_a values of these acids are : acetic 4.74; benzoic 4.18 and formic 3.68.

Sol.

76. Calculate the pH of 0.1 M solution of (i) NaHCO_3 , (ii) Na_2HPO_4 and (iii) NaH_2PO_4 . Given that ;



Sol.

77. Mixtures of solution. Calculate the pH of the following solution. $\text{K}_1 = 7.5 \times 10^{-3} \text{ M}$;

$$\text{K}_2 = 6.2 \times 10^{-8} \text{ M}; \quad \text{K}_3 = 1.0 \times 10^{-12} \text{ M}$$

(A) 40 ml of 0.050 M Na_2CO_3 + 50 ml of 0.040 M HCl ;

(B) 40 ml of 0.020 M Na_3PO_4 + 40 ml of 0.040 M HCl ;

(C) 50 ml of 0.10 M Na_3PO_4 + 50 ml of 0.10 M NaH_2PO_4

(D) 40 ml of 0.10 M H_3PO_4 + 40 ml of 0.10 M Na_3PO_4 .

Sol.

78. A buffer solution was prepared by dissolving 0.05 mol formic acid & 0.06 mol sodium formate in enough water to make 1.0 L of solution. K_a for formic acid is 1.80×10^{-4}

(a) Calculate the pH of the solution.

(b) If this solution were diluted to 10 times its volume, what would be the pH?

(c) If the solution in (b) were diluted to 10 times its volume, what would be the pH?

Sol.

79. If 0.0050 mol NaHCO_3 is added to 1 litre of a buffered solution at pH 8.00, how much material will exist in each of the three forms H_2CO_3 , HCO_3^- and CO_3^{2-} ? For H_2CO_3 , $K_1 = 5 \times 10^{-7}$, $K_2 = 5 \times 10^{-13}$.

Sol.

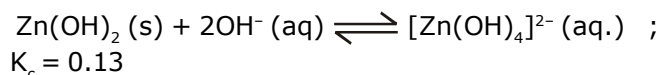
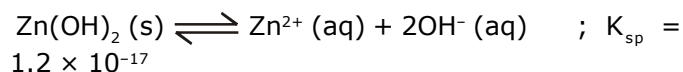
80. The indicator phenol red is half in the ionic form when pH is 7.2. If the ratio of the undissociated form to the ionic form is 1 : 5, find the pH of the solution. With the same pH for solution, if indicator is altered such that the ratio of undissociated form to dissociated form becomes 1 : 4, find the pH when 50% of the new indicator is in ionic form.

Sol.

81. An organic monoprotic acid [0.1M] is titrated against 0.1 M NaOH. By how much does the pH change between one fourth and three fourth stages of neutralization? If at one third stage of neutralization, the pH is 4.45 what is the dissociation constant of the acid? Between what stages of neutralisation may the pH change by 2 units?

Sol.

82. The salt Zn(OH)_2 is involved in the following two equilibria,



Calculate the pH of solution at which solubility is minimum.

Sol.

83. Predict whether or not AgCl will be precipitated from a solution which is 0.02 M in NaCl and 0.05 M in KAg(CN)_2 . Given $K_{\text{inst}}(\text{Ag(CN)}_2^-) = 4.0 \times 10^{-19} \text{ M}^2$ and $K_{\text{sp}}(\text{AgCl}) = 2.8 \times 10^{-10} \text{ M}^2$.

Sol.

84. Show that solubility of a sparingly soluble salt $\text{M}^{2+} \text{A}^{2-}$ in which A^{2-} ions undergoes hydrolysis is given by

$$S = \sqrt{K_{\text{sp}} \left(1 + \frac{[\text{H}^+]}{K_2} + \frac{[\text{H}^+]^2}{K_1 K_2} \right)}$$

where K_1 and K_2 are the dissociation constant of acid H_2A . K_{sp} is solubility product of MA.

Sol.

EXERCISE – IV**PREVIOUS YEARS PROBLEMS****LEVEL – I****JEE MAIN**

1. The solubility of $\text{Mg}(\text{OH})_2$ is x mole/ltr. then its solubility product is - **[AIEEE-2002]**

(A) x^3 (B) $5x^3$
(C) $4x^3$ (D) $2x^2$

Sol.

2. The solubility in water of a sparingly soluble salt AB_2 is $1.0 \times 10^{-5} \text{ mol L}^{-1}$. Its solubility product will be - **[AIEEE-2003]**

(A) 1×10^{-15} (B) 1×10^{-10}
(C) 4×10^{-15} (D) 4×10^{-10}

Sol.

3. The molar solubility (in mol L^{-1}) of a sparingly soluble salt MX_4 is 's'. The corresponding solubility product is K_{SP} . 's' is given in terms of K_{SP} by the relation - **[AIEEE-2004]**

(A) $s = (K_{\text{SP}}/128)^{\frac{1}{4}}$ (B) $s = (128K_{\text{SP}})^{\frac{1}{4}}$
(C) $s = (256K_{\text{SP}})^{\frac{1}{5}}$ (D) $s = (K_{\text{SP}}/256)^{\frac{1}{5}}$

Sol.

4. The solubility product of a salt having general formula MX_2 , in water is 4×10^{-12} . The concentration of M^{2+} ions in the aqueous solution of the salt is - **[AIEEE-2005]**

(A) $1.0 \times 10^{-4} \text{ M}$ (B) $2.0 \times 10^{-6} \text{ M}$
(C) $4.0 \times 10^{-10} \text{ M}$ (D) $1.6 \times 10^{-4} \text{ M}$

Sol.

5. The first and second dissociation constants of an acid H_2A are 1.0×10^{-5} & 5.0×10^{-10} respectively. The overall dissociation constant of the acid will be - **[AIEEE-2007]**

(A) 5.0×10^{-5} (B) 5.0×10^{15}
(C) 5.0×10^{-15} (D) 0.2×10^5

Sol.

6. The pK_a of a weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA in which 50% of the acid is ionized is- **[AIEEE-2007]**

(A) 4.5 (B) 2.5
(C) 9.5 (D) 7.0

Sol.

7. In a saturated solution of the sparingly soluble strong electrolyte AgIO_3 (molecular mass = 283) the equilibrium which sets in is -



If the solubility product K_{SP} of AgIO_3 at a given temperature is 1.0×10^{-8} , what is the mass of AgIO_3 contained in 100 ml of its saturated solution? **[AIEEE-2007]**

(A) $28.3 \times 10^{-2} \text{ g}$ (B) $2.83 \times 10^{-3} \text{ g}$
(C) $1.0 \times 10^{-7} \text{ g}$ (D) $1.0 \times 10^{-4} \text{ g}$

Sol.

8. The pK_a of a weak acid, HA, is 4.80. The pK_b of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be - **[AIEEE-2008]**

(A) 4.79 (B) 7.01
(C) 9.22 (D) 9.58

Sol.

9. Solid $\text{Ba}(\text{NO}_3)_2$ is gradually dissolved in a $1.0 \times 10^{-4} \text{ M}$ Na_2CO_3 solution. At what concentration of Ba^{2+} will a precipitate begin to form ?

(K_{sp} for $\text{BaCO}_3 = 5.1 \times 10^{-9}$) [AIEEE-2009]

- (A) $5.1 \times 10^{-5} \text{ M}$ (B) $8.1 \times 10^{-8} \text{ M}$
(C) $8.1 \times 10^{-7} \text{ M}$ (D) $4.1 \times 10^{-5} \text{ M}$

Sol.

10. In aqueous solution the ionization constants for carbonic acid are $K_1 = 4.2 \times 10^{-7}$ and $K_2 = 4.8 \times 10^{-11}$. Selection the correct statement for a saturated 0.034 M solution of the carbonic acid. [AIEEE-2010]

- (A) The concentration of H^+ is double that of CO_3^{2-}
(B) The concentration of CO_3^{2-} is 0.034 M.
(C) The concentration of CO_3^{2-} is greater than that of HCO_3^-
(D) The concentration of H^+ and HCO_3^- are approximately equal.

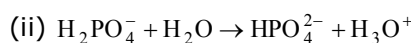
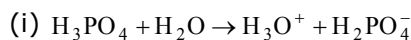
Sol.

11. Solubility product of silver bromide is 5.0×10^{-13} . The quantity of potassium bromide (molar mass taken as 120 g mol^{-1}) to be added to 1 litre of 0.05 M solution of silver nitrate to start the precipitation of AgBr is [AIEEE-2010]

- (A) $5.0 \times 10^{-8} \text{ g}$ (B) $1.2 \times 10^{-10} \text{ g}$
(C) $1.2 \times 10^{-9} \text{ g}$ (D) $6.2 \times 10^{-5} \text{ g}$

Sol.

12. Three reactions involving H_2PO_4^- are given below: [AIEEE-2010]



In which of the above does H_2PO_4^- act as an acid?

- (A) (i) Only (B) (ii) Only
(C) (ii) and (iii) (D) (iii) only

Sol.

13. At 25°C , the solubility product of $\text{Mg}(\text{OH})_2$ is 1.0×10^{-11} . At which pH, will Mg^{2+} ions start precipitating in the form of $\text{Mg}(\text{OH})_2$ from a solution of 0.001 M Mg^{2+} ions ? [AIEEE-2010]

- (A) 8 (B) 9
(C) 10 (D) 11

Sol.

14. The pH of a 0.1 molar solution of the acid HQ is 3. The value of the ionization constant, K_a of this acid is – [AIEEE-2012]

- (A) 1×10^{-3} (B) 1×10^{-5}
(C) 1×10^{-7} (D) 3×10^{-1}

Sol.

15. How many litres of water must be added to litre of an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2? [AIEEE-2013]

- (A) 2.0 L (B) 9.0 L
(C) 0.1 L (D) 0.9 L

Sol.

LEVEL – II

JEE ADVANCED

1. The degree of dissociation of water at 25°C is $2 \times 10^{-7} \%$ and density is 1.0 g cm^{-3} . The ionization constant for water is - **[IIT-1995]**

(A) 1.0×10^{-14} (B) 2.0×10^{-16}
(C) 1.0×10^{-16} (D) 1.0×10^{-8}

Sol.

2. What will be the resultant pH when 200 ml aqueous solution of HCl (pH = 2.0) is mixed with 300 ml of an aqueous solution of NaOH (pH=12.0)? **[JEE 1998]**

Sol.

3. A buffer solution can be prepared from a mixture of - **[IIT-1999]**

(A) Sodium acetate and acetic acid in water
(B) Sodium acetate and hydrochloric acid in water
(C) ammonia and ammonium chloride in water
(D) ammonia and sodium hydroxide in water

Sol.

4. The solubility of Pb(OH)_2 in water is $6.7 \times 10^{-6} \text{ M}$. Calculate the solubility of Pb(OH)_2 in a buffer solution of pH = 8. **[JEE '1999]**

Sol.

5. The pH of 0.1 M solution of the following salts increases in the order **[JEE 1999]**

(A) $\text{NaCl} < \text{NH}_4\text{Cl} < \text{NaCN} < \text{HCl}$
(B) $\text{HCl} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{NaCN}$
(C) $\text{NaCN} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{HCl}$
(D) $\text{HCl} < \text{NaCl} < \text{NaCN} < \text{NH}_4\text{Cl}$

Sol.

6. An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 mL. The volume of 0.1 N NaOH required to completely neutralise 10 mL of this solution is : **[JEE 2001]**

(A) 40 mL (B) 20 mL
(C) 10 mL (D) 4 mL

Sol.

7. For sparingly soluble salt $ApBq$, the relationship of its solubility product (L_s) with its solubility (S) is [JEE 2001]
 (A) $L_s = S^{p+q}$, $p^p \cdot q^q$ (B) $L_s = S^{p+q}$, $p^p \cdot q^p$
 (C) $L_s = S^{p+q}$, $p^p \cdot q^q$ (D) $L_s = S^{p+q}$, $(p \cdot q)^{p+q}$

Sol.

8. 500 ml of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 25°C
 (a) Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.
 (b) If 6 g of NaOH is added to the above solution, determine final pH. Assume there is no change in volume on mixing. K_a of acetic acid is 1.75×10^{-5} M. [JEE 2002]

Sol.

9. A solution which is 10^{-3} M each in Mn^{2+} , Fe^{2+} , Zn^{2+} and Hg^{2+} is treated with 10^{-16} M sulphide ion. If K_{sp} , MnS , FeS , ZnS and HgS are 10^{-15} , 10^{-23} , 10^{-20} and 10^{-54} respectively, which one will precipitate first? [JEE 2003]
 (A) FeS (B) MnS
 (C) HgS (D) ZnS

Sol.

10. Will the pH of water be same at 4°C and 25°C? Explain. [JEE 2003]

Sol.

11. HX is a weak acid ($K_a = 10^{-5}$). It forms a salt NaX (0.1 M) on reacting with caustic soda. The degree of hydrolysis of NaX is [JEE 2004]
 (A) 0.01 % (B) 0.0001%
 (C) 0.1% (D) 0.5%

Sol.

12. 0.1 M of HA is titrated with 0.1 M NaOH, calculate the pH at end point. Given $K_a(\text{HA}) = 5 \times 10^{-6}$ and $\alpha \ll 1$.
[JEE 2003]

Sol.

13. CH_3NH_2 (0.1 mole, $K_b = 5 \times 10^{-4}$) is added to 0.08 moles of HCl and the solution is diluted to one litre, resulting hydrogen ion concentration is
[JEE 2005]

- (A) 1.6×10^{-11} (B) 8×10^{-11}
(C) 5×10^{-5} (D) 2×10^{-2}

Sol.

14. $\text{Ag}^+ + \text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)]^+ ; k_1 = 3.5 \times 10^{-3}$
 $[\text{Ag}(\text{NH}_3)]^+ + \text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+ ;$
 $k_2 = 1.7 \times 10^{-3}$ [JEE 2006]
then the formation constant of $[\text{Ag}(\text{NH}_3)_2]^+$ is
(A) 6.08×10^{-6} (B) 6.08×10^6
(C) 6.08×10^{-9} (D) None of these

Sol.

15. The species present in solution when CO_2 is dissolved in water: [JEE 2006]

- (A) $\text{CO}_2, \text{H}_2\text{CO}_3, \text{HCO}_3^-, \text{CO}_3^{2-}$
(B) $\text{H}_2\text{CO}_3, \text{CO}_3^{2-}$
(C) $\text{CO}_3^{2-}, \text{HCO}_3^-$
(D) $\text{CO}_2, \text{H}_2\text{CO}_3$

Sol.

16. Solubility product constant (K_{sp}) of salts of types MX, MX_2 and M_3X at temperature 'T' are 4.0×10^{-8} , 3.2×10^{-14} and 2.7×10^{-15} , respectively. Solubilities (mol. dm^{-3}) of the salts at temperature 'T' are in the order [JEE 2008]

- (A) $\text{MX} > \text{MX}_2 > \text{M}_3\text{X}$ (B) $\text{M}_3\text{X} > \text{MX}_2 > \text{MX}$
(C) $\text{MX}_2 > \text{M}_3\text{X} > \text{MX}$ (D) $\text{MX} > \text{M}_3\text{X} > \text{MX}_2$

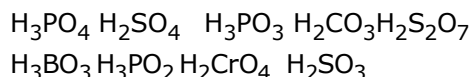
Sol.

17. 2.5 mL of $\frac{2}{5}$ M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°C) is titrated with $\frac{2}{15}$ M HCl in water at 25°C . The concentration of H^+ at equivalence point is ($K_w = 1 \times 10^{-14}$ at 25°C)
[JEE 2008]

- (A) 3.7×10^{-13} M (B) 3.2×10^{-7} M
(C) 3.2×10^{-2} M (D) 2.7×10^{-2} M

Sol.

20. The total number of diprotic acids among the following is **[IIT-2010]**



Sol.

18. The dissociation constant of a substituted benzoic acid at 25°C is 1.0×10^{-4} . The pH of a 0.01 M solution of its sodium salt is :

[JEE 2009]

Sol.

21. In 1 L saturated solution AgCl [$K_{sp}(\text{AgCl}) = 1.6 \times 10^{-10}$], 0.1 mol of CuCl [$K_{sp}(\text{CuCl}) = 1.0 \times 10^{-6}$] is added. The resultant concentration of Ag^+ in the solution is 1.6×10^{-x} . The value of "x" is **[JEE 2011]**

Sol.

19. Aqueous solutions of HNO_3 , KOH, CH_3COOH , and CH_3COONa of identical concentrations are provided. The pair(s) of solutions which form a buffer upon mixing is(are). **[JEE 2010]**

- (A) HNO_3 and CH_3COOH
(B) KOH and CH_3COONa
(C) HNO_3 and CH_3COONa
(D) CH_3COOH and CH_3COONa

Sol.

22. The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12} at 298 K. The solubility (in mol/L) of Ag_2CrO_4 in a 0.1 M AgNO_3 solution is **[IIT-2013]**

- (A) 1.1×10^{-11} (B) 1.1×10^{-10}
(C) 1.1×10^{-12} (D) 1.1×10^{-9}

Sol.

23. The initial rate of hydrolysis of methyl acetate (1M) by a weak acid (HA, 1M) is $1/100^{\text{th}}$ of a strong acid (HX, 1M) at 25°C. The K_a of HA is **[IIT-2013]**

- (A) 1×10^{-4} (B) 1×10^{-5}
(C) 1×10^{-6} (D) 1×10^{-3}

24. The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12} at 298 K. The solubility (in mol/L) of Ag_2CrO_4 in a 0.1 M AgNO_3 solution is

- (A) 1.1×10^{-11} (B) 1.1×10^{-10}
(C) 1.1×10^{-12} (D) 1.1×10^{-9}

Answers

Answer Ex-I

OBJECTIVE PROBLEMS (JEE MAIN)

- | | | | | | | | |
|-------|-------|-------|-------|------------------------|-------------------|-------|-------|
| 1. A | 2. C | 3. C | 4. B | 5. B | 6. C | 7. B | 8. D |
| 9. B | 10. A | 11. D | 12. D | 13. B | 14. B | 15. D | 16. D |
| 17. C | 18. D | 19. C | 20. C | 21. B | 22. A | 23. D | 24. D |
| 25. D | 26. A | 27. C | 28. B | 29. A | 30. A | 31. C | 32. D |
| 33. B | 34. A | 35. A | 36. B | 37. D | 38. C | 39. C | 40. C |
| 41. A | 42. A | 43. C | 44. A | 45. A-P, B-Q, C-S, D-R | 46. A-S, B-S, C-Q | | |
| 47. A | 48. D | 49. A | 50. C | | | | |

Answer Ex-II

OBJECTIVE PROBLEMS (JEE ADVANCED)

- | | | | | | | | |
|--------|--------|----------|----------|----------|-------|-------|-------|
| 1. B,C | 2. B,C | 3. A,B,C | 4. A,B,C | 5. A,B,C | 6. A | 7. B | 8. D |
| 9. C | 10. B | 11. A | 12. D | 13. C | 14. A | 15. D | 16. B |
| 17. A | 18. A | 19. C | 20. B | | | | |

Answer Ex-III

SUBJECTIVE PROBLEMS (JEE ADVANCED)

- | | | |
|--|------------------------|--------------------------|
| 1. 0.6×10^{-7} | 2. 6.022×10^7 | 3. 2.31×10^{-8} |
| 4. (a) 1 (b) 2.87 (c) 11.13 (d) 0.522 (e) 6.97 (f) 7 (g) 11.30 (h) 9 (i) 1 (j) 3 (k) 6.01 (l) 6.97 | | |
| 5. (a) $K_a = 10^{-8}$ (b) $K_b = 10^{-6}$ | | |

6. 10 7. 170.4 8. 0.556 9. 1.11×10^{-4} 10. 4.87
11. $[H^+] = 1.612 \times 10^{-2} M$, $[CHCl_2COO^-] = 6.126 \times 10^{-3} M$ 12. $[H^+] = 10^{-3} M$, $[CH_3COO^-] = 3.6 \times 10^{-4} M$, $[C_7H_5O_2^-] = 6.4 \times 10^{-4} M$
13. 2.61 14. $[H^+] = [H_2PO_4^-] = 2.7 \times 10^{-3}$, $[HPO_4^{2-}] = 10^{-8}$, $[PO_4^{3-}] = 3.7 \times 10^{-19}$ 15. pH = 11.46, $[enH_2^{2+}] = 7.1 \times 10^{-8}$
16. 0.2116 M, 0.1884 M, 0.0116 M, 0 17. 0.027M, 0.073 M, 0.027M, $10^{-5} M$ 18. 10.07
19. 10 20. 9.0×10^{-6} 21. 4.74 22. 0.05 mol 23. 9.56
24. (a) pH = 9.239 (b) Lowered (c) pH = 4.699 25. 8.7782 26. 9.7324
27. $[HIn] = 28.57 \%$ 28. (b) & (c) 29. Methyl red, one with pH = 5.22 as mid point of colour change
30. 85.71 % 31. $\Delta pH = 0.954$ 32. $[OH^-] = 6.664 \times 10^{-6}$ 33. pH = 4.477
34. $K_b = 6.25 \times 10^{-10}$ 35. 0.56%, pH = 7 36. 1.667% 37. 0.26% 38. 4%
39. 10^{-6} , 10^{-8} 40. pH = 10.43 41. 8.34 42. 4.19 43. (a) 6 (b) 1×10^{-5} 44. $5.12 \times 10^{-6} M$
45. 8.71 46. 4.98 47. $pK_a = 6.1$ 48. 2.37×10^{-6} 49. $K_b = 1.8 \times 10^{-5}$, 5.27 50. 8.73
51. (i) 2.85 (ii) 4.0969 (iii) 4.5229 (iv) 4.699 (v) 5.301 (vi) 8.699 52. QX_2 is more soluble 53. 1.6×10^{-8}
54. $[Cu^+] = 5 \times 10^{-11} M$ 55. 3.4×10^{-11} 56. 2.6×10^{-16} 57. $1 \times 10^{-18} M$
58. $1 \times 10^{-5} \text{ mol/L}$ 59. $5 \times 10^{-10} M$ 60. 12 mg
61. (a) no ppt will occur (b) a ppt will form 62. 1.6×10^{-3} 63. 2.49×10^{-5}
64. 2.1×10^{-5} 65. $9 \times 10^{-7} M$, $4 \times 10^{-7} M$ 66. $[F^-] = 3 \times 10^{-3} M$ 67. 19.5 kg

68. $K_d = \frac{1}{K_f} = 4.8 \times 10^{-4}$ 69. $2.8 \times 10^{-3} \text{ M}$ 70. error = 1% 71. $V = 2.77 \times 10^4 \text{ litre}$
72. (a) 13.1 (b) 0.13 M 73. (a) 2.12 (b) 4.66 (c) 7.2 (d) 12 74. 5.158
75. acetic acid, salt-acid molar ratio 1.8 : 1 76. 8.35, 9.60, 4.66 77. (a) 8.34 (b) 4.66 (c) 9.6 (d) 7.20
78. (a) pH = 3.83 (b) pH = 3.85, (c) = 3.99 79. $[\text{H}_2\text{CO}_3] = 9.85 \times 10^{-6} \text{ M}$; $[\text{HCO}_3^-] = 4.9 \times 10^{-4}$ $[\text{CO}_3^{2-}] = 2.45 \times 10^{-8}$
80. pH = 7.3 81. 0.9542 82. 9.99, $s = 10^{-9} \text{ M}$ 83. ppt. will occur

Answer Ex-IV**PREVIOUS YEARS PROBLEMS****LEVEL – I****JEE MAIN**

1. C 2. C 3. D 4. A 5. C 6. C 7. B
8. B 9. A 10. D 11. C 12. B 13. C 14. B
15. B

LEVEL – II**JEE ADVANCED**

1. B 2. pH=11.3010 3. AC 4. $s = 1.203 \times 10^{-3} \text{ M}$ 5. B
6. A 7. A 8. (a) 0.0175% (b) 4.757 9. C
10. No it will be > 7 11. A 12. pH = 9 13. B
14. A 15. A 16. D 17. D 18. pH = 8 19. C,D
20. 6 21. 7 22. B 23. A 24. B

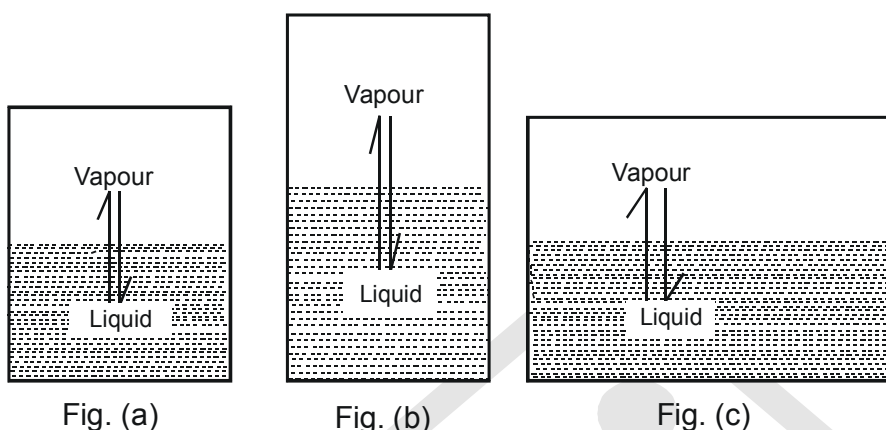
LIQUID SOLUTION

CONCEPT OF VAPOUR PRESSURE

When a pure liquid is kept in closed vessel (in which no air is present) the liquid evaporates to give the vapours. After sometime a dynamic equilibrium is established between liquid and vapours. *The pressure that the vapours exert at equilibrium on the walls of the container or on the surface of the liquid is called the vapour pressure of the liquid at that temperature, Figure (a).*

Case 1:

What would happen to the vapour pressure of the liquid if we take a bigger container, Figure (b) or a wider container, Figure (c).

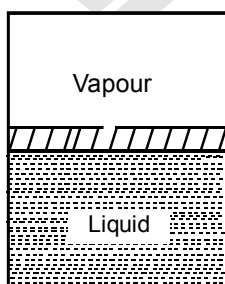


Key concept:

When the liquid is in equilibrium with vapours, $\text{Liquid} \rightleftharpoons \text{Vapours}$, the K_p of the system is $K_p = P_v$, where P_v is the vapour pressure. We know that K_p for a given chemical equilibrium is a constant and only depends on temperature. Therefore the vapour pressure of the liquid is a constant and does not depend on the nature of the vessel used and that it only depends on temperature.

Case 2:

Take a vessel with the same liquid as in case 1 and cover it with a glass plate (of negligible weight) having a hole in it. Would the vapour pressure be the same now?



Key concept:

Well, the liquid system is the same and the temperature is also same. Therefore the vapour pressure should be same. The vapour pressure of a liquid is independent of the surface area exposed on top of the liquid surface provided the surface area exposed should not be zero.

TYPE OF SOLUTIONS

Solutions can have continuously variable compositions, and they are homogeneous on a scale beyond the size of individual molecules. This definition can be used to cover a wide variety of systems, including ordinary solution such as alcohol in water or HClO_4 in benzene and even solution of large proteins in aqueous salt solutions. It is also useful sometimes to consider some colloidal suspensions undergoing Brownian motion as solutions, and there are solid solutions where one solid is uniformly dissolved in another.

SOME EXAMPLES OF SOLUTIONS			
Solute	Solvent	Name of Type	Heat of Solution per Mole of Solute (kJ)
$\text{O}_{2(g)}$	$\text{N}_{2(g)}$	Gaseous	0
Toluene	Benzene	Ideal	– 0.1
Acetone	Chloroform	Non ideal	5
$\text{NaCl}_{(s)}$	$\text{H}_2\text{O}_{(l)}$	Ionic	– 3.9
$\text{H}_2\text{SO}_{4(l)}$	$\text{H}_2\text{O}_{(l)}$	Ionic	95.3
Positive values are heat released.			

Most solutions can be described as having a majority called a *solvent* and one or more minority ingredients called *solutes*. The solvent is usually a liquid, whereas solutes can be solids, liquids, or gases. Solutions can be distinguished from compounds by the kind of interaction between ingredients. Compounds form as a result of interactions between relatively permanent partners, while the interactions in solutions involve continuously variable sets of solute and solvent molecules, and this interaction is widely distributed among a large and solvent molecules. Above table gives some examples of solutions and for each we want to be able to understand why the solute dissolves in the solvent.

$\text{O}_{2(g)}$ in $\text{N}_{2(g)}$

This first example is; of course, of one gas dissolved in another all gases dissolve in each other in all proportions. The reason for this is that solute and solvent do not interact. This is illustrated in fig. which shows that

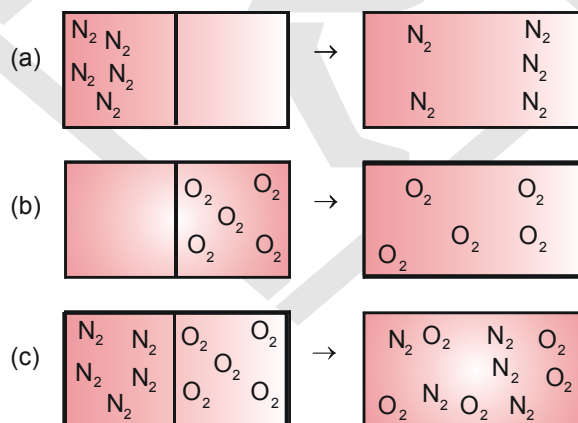


Fig. The expansion of gas as illustrated by a solution of N_2 and O_2 (diagrammatic). The expansions of (a) N_2 and of (b) O_2 are shown to be equivalent to forming (c) a solution of N_2 and O_2 .

the process of two gases dissolving in each other is equivalent to expansion of each gas into the larger volume without any interaction with the other. As we can see from this figure and as we also know from our daily experience, this mixing takes place spontaneously. In a gas, the high thermal energy that the molecules possess keeps them always on the move. This motion allows them to distribute themselves between the two bulbs in an arrangement with the greatest probability of occurring. That distribution results in equal O_2 or N_2 partial pressures in each bulb with the N_2 and O_2 completely mixed. It is important to note that the energy of the system has not changed, only the way in which the molecules are distributed; that is, the entropy, S of the system has changed.

On the molecular level, entropy is a measure of randomness; a maximum in entropy corresponds to the

most probable distribution on a statistical basis.

While the mixing of ideal gases is controlled by entropy, the mixing of molecules that interact with each other can surely be controlled by energy. In the mixing process the molecular interactions can either cause the energy to increase or decrease. Chemical changes that are very exothermic show a large decrease in energy and enthalpy; as a result, they are spontaneous. However, most solutes dissolve in solvents because mixing increases the system's entropy ($\Delta S > 0$); that it is more probable for the solutes to dissolve in the solvents than for them to remain separate as pure substances.

Toluene in Benzene

These two similar liquids readily dissolve in each other. At first glance we might think this solution shows the same pattern of mixing as do two ideal gases, but this cannot be correct since the molecules in a liquid interact with each other very strongly. The key to this solution is that the molecules of the two liquids have similar electronic structures and similar sizes. As a result, the benzene – benzene, benzene – toluene and toluene – toluene interactions are very similar. A toluene molecule, as an approximation, does not know if it is surrounded by other toluene molecule or by benzene molecules. As we might expect, there is a very negligible *heat of solution*. These two liquids completely dissolve one in the other and are an *ideal solution*. These two liquids completely dissolve one in what is called an *ideal solution*. The entropy gained by mixing toluene with benzene is the same as that gained by mixing two ideal gases. Solvent and solute molecules have no specific interaction with each other that do not have with molecules of their own kind. As a result the molecules distribute randomly in the solution and the change in entropy upon mixing is the same as that for two ideal gases.

Acetone in Chloroform

These two liquids are not very similar; the attraction of acetone and chloroform molecules for each other is quite different from the attraction of the like molecules for each other. When acetone and chloroform are mixed heat is given off so they do not form an ideal solution.

Even so, they are completely miscible. In some cases when the molecules in two liquids have quite different interactions, they may not be completely miscible. For example water and acetone are completely miscible, but water and chloroform are not. The property of liquids used to characterize solvent – solute interactions is called *polarity*. Polarity measures the small separation of positive and negative charges in molecules. Water is considered to be the most polar of the common solvents, as attested by the fact that it is the best solvent for ionic solutes. Acetone has an intermediate value of polarity, and chloroform is much less polar than acetone. Molecules interact very differently with molecules of widely different degrees of polarity than they do with others of their own kind. This difference in interaction leads to *immiscibility*.

NaCl(s) in H₂O(l)

The compound NaCl has the high melting temperature characteristic of most ionic solids. It consists of Na⁺ and Cl⁻ ions. When NaCl dissolves in water, these ions interact with the water molecules and separate. The interaction with water is particularly large for positively charged ions, and the Na⁺ is surrounded by six closely bound water molecules. Ions surrounded by closely bound water molecules are said to be hydrated. For salts such as CaCl₂ or AlCl₃, the water molecules interact even more strongly with their cations and they give off heat when they dissolve. For NaCl the energy required to separate the Na⁺ and Cl⁻ ions is nearly balanced by the energy of interaction between the water and the ions. Salts such as NaNO₃ or NH₄NO₃ make their solutions colder when they dissolve to produce hydrated Na⁺, NH₄⁺ and NO₃⁻ ions. The entropy of solution for an ionic solid would never be expected to be as high as its entropy of vaporization; nevertheless, salts such as NaCl and NaNO₃ dissolve in water because there is a greater probability of finding them in the form of separated and hydrated ions than packed neatly in a solid. Again entropy is the controlling factor.

H₂SO₄(ℓ) in H₂O(ℓ)

Almost every chemist knows that H₂SO₄ gives off a large amount of heat when it dissolves in water. While pure H₂SO₄ does not contain ions, as indicated by that fact that it is a liquid at room temperature, in dilute aqueous solutions it completely ionizes into H⁺ and SO₄²⁻. Its high heat of solution arises largely from the heat of hydration of H⁺. Other proton-yielding solutes like HCl(g) and HClO₄(ℓ) also have large, positive heats of solution so they readily dissolve in water.

RAOULT'S LAW

It states that on adding a non-volatile solute to a volatile solvent, forming an ideal solution, the vapour pressure of the solvent is lowered and it is directly proportional to the mole fraction of the solute in the solution.

Case 1:

Let us add a non-volatile solute that dissolves in the liquid and observe the effect on vapour pressure. As the non-volatile substance dissolves, some of the particles would be present on the surface of the liquid, thereby decreasing the number of solvent particles present per unit area of the surface.

Key concept:

The vapour pressure of a liquid does not depend on the surface area of the solvent exposed but only depends on the no. of solvent molecules present per unit area on the surface (which decreases only on dissolving a solute).

The rate at which the solvent molecules leave the surface is proportional to the no. of solvent molecules per unit area on the surface, which in turn is proportional to the mole fraction of the solvent.

Rate of vaporization = $k X_{\text{solvent}}$

Where k is proportionality constant and X_{solvent} is the mole fraction of the solvent in the solution. The rate with which vapour molecules condense is proportional to their concentration in the gaseous phase, which is proportional to their partial pressure.

Rate of condensation = $k' P_{\text{solvent}}$

Where k' is proportionality constant and P_{solvent} is vapour pressure of the solvent. At equilibrium,

$$k X_{\text{solvent}} = k' P_{\text{solvent}} \quad (\because \text{both rates are equal})$$

$$\text{or} \quad P_{\text{solvent}} = \frac{k}{k'} X_{\text{solvent}}$$

In case of pure solvent, $X_{\text{solvent}} = 1$ and $P_{\text{solvent}} = \frac{k}{k'}$. If the pure vapour pressure of the solvent is P° , then

$$\frac{k}{k'} = P^\circ.$$

$$\therefore P = X_{\text{solvent}} P^\circ.$$

This is the mathematical expression of the Raoult's law.

Case 2:

Let us mix two volatile liquids. Assuming that both of them obey Raoult's law, $P_{\text{total}} = X_A P_A^\circ + X_B P_B^\circ$,

where X_A is mole fraction of component A in the solution and P_A° is its pure vapour pressure and

likewise for B. This also implies that $P_A = X_A P_A^\circ$ and $P_B = X_B P_B^\circ$, where P_A and P_B are the partial pressures of A and B. In this case, definition of an ideal solution changes. Since both of them obey Raoult's law, one cannot assume any one of them to be in lesser amount.

Key concept:

An ideal solution is a solution in which A – A interactions, B – B interactions and A – B interaction are same (provided that ΔH_{mix} and $\Delta V_{mix} = 0$).

Case 3:

Is the vapour pressure of a solution of a non – volatile solute in a volatile liquid also a constant?

As we know that the concentration of a solution is not a constant in this case. Therefore, this system does not have a K_p . It means that the vapour pressure of a solution is not a constant. To make the calculations involving liquid solution does not effectively change the concentration of the solution.

Key concept:

The system of solution – vapour also has a constant K_p and therefore a constant vapour pressure.

COLLIGATIVE PROPERTIES

These are the properties of solutions which depend upon the relative number of solute particles (molecules or ions) but not upon their nature. These are relative lowering of vapour pressure, elevation of boiling point, depression in freezing point and the osmotic pressure arising due to the presence of a non – volatile solute.

Key concept:

In dilute solutions these properties depend only on the number of solute particles present and not on their identity. For this reason they are called colligative properties (denoting depending on the collection).

We shall assume throughout the following that.

- (i) The solute is non – volatile.
- (ii) The solute does not dissolve in the solid solvent (the pure solid separates when the solution is frozen).

RELATIVE LOWERING OF VAPOUR PRESSURE

According to the Raoult's law, $P_{\text{solvent}} = X_{\text{solvent}} P_{\text{solvent}}^{\circ}$

Where P_{solvent} is the vapour pressure of the liquid solution, X_{solvent} is its mole fraction in the solution and $P_{\text{solvent}}^{\circ}$ is the pure vapour pressure.

$$\therefore X_{\text{solvent}} = \frac{P_{\text{solvent}}}{P_{\text{solvent}}^{\circ}}$$

$$1 - X_{\text{solvent}} = 1 - \frac{P_{\text{solvent}}}{P_{\text{solvent}}^{\circ}} = \frac{P_{\text{solvent}}^{\circ} - P_{\text{solvent}}}{P_{\text{solvent}}^{\circ}} \quad \text{or} \quad X_{\text{solute}} = \frac{P^{\circ} - P}{P^{\circ}}$$

Above expression is called as the relative lowering of vapour pressure (fraction of the vapour pressure lowered). Thus, the relative lowering of vapour pressure of a solvent due to the dissolution of a non-volatile solute in it is equal to the molefraction of the solute in the solution. This is another form of the Raoult's law.

Key concept:

The molefraction of any substance does not change with temperature. So the molefraction of the solute (X_{solute}) does not change with temperature. Then, according to above expression the relative lowering of the vapour pressure should be independent of temperature. This is found to be so only for dilute solutions. Therefore, the Raoult's law, in this form, is applicable to the dilute solutions of non-volatile and non-electrolytic solutes only.

OSTWALD – WALKER EXPERIMENT

When air is passed through any gas, the gas diffuses into the air due to the principle of diffusion till the pressure of the gas in the air is equal to that of the gas outside. Therefore as air is passed through the solution, it absorbs the vapours of the solvent till the pressure of the solvent vapours in the air is P (vapour pressure of solvent in the solution).

$$\therefore \text{Mass of vapour absorbed or loss in weight of solution} = \frac{PV_m}{RT}$$

Where, P = pressure of the solvent vapours, V = volume available for vapours in the solution bulb, T = temperature of the bulb and m = molecular weight of the solvent.

As the air passes through the solvent, the pressure difference of the vapours in the air and outside is $P^\circ - P$. So the air absorbs this amount of vapours and gets saturated.

$$\therefore \text{Loss in weight of solvent bulb} = \frac{(P^\circ - P)V_m}{RT}$$

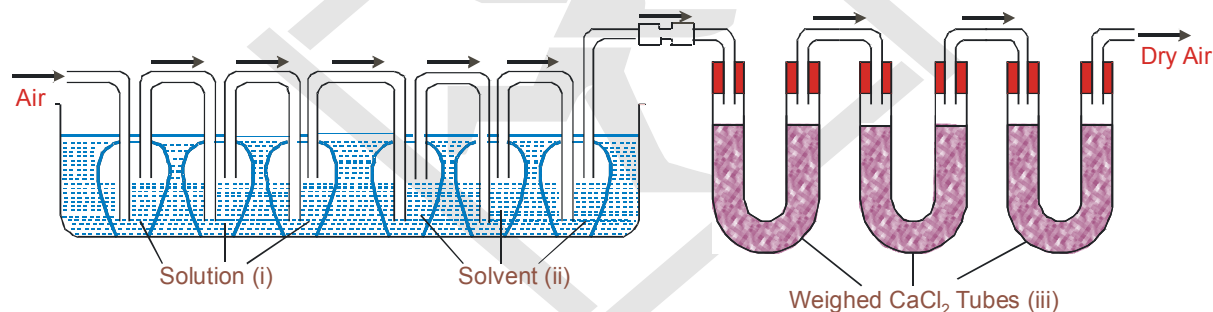
As the sum of the losses of weight in the two containers is equal to the gain in weight of CaCl_2 ,

$$\text{Gain in weight of } \text{CaCl}_2 \text{ filled tubes} = \frac{P^\circ V_m}{RT}$$

$$\therefore \frac{\text{Loss in wt. of solvent}}{\text{Gain in wt. of } \text{CaCl}_2} = \frac{P^\circ - P}{P^\circ}$$

Method

In this method a stream of dry air is passed successively through (i) a solution (ii) the pure solvent (water) and (iii) a reagent (anhydrous CaCl_2) which can absorb the vapours of the solvent. The complete assembly is shown in figure, given below:



The first three bulbs contain a weighed amount of the solution under examination and the next three bulbs contain a weighed amount of the pure solvent. A weighed amount of CaCl_2 is taken in the set of U – tubes at the end. All the bulbs are at the same temperature and the volume available for the vapours in the solution and solvent bulbs are same temperature and the volume available for the vapours in the solution and solvent bulbs are same.

Key concept:

It is designed in order to calculate the relative lowering of vapour pressure of a solvent due to a non – volatile solute.

Illustration

0.5 g of a non-volatile organic substance was dissolved in 100 mL of CCl_4 at 30°C . The vapour pressure of the solution was found to be 141.9 torr. Calculate the molar mass of the substance if the vapour pressure of CCl_4 at 30°C is 143 torr and its density is 1.58 g mL^{-1} .

Solution:
$$\frac{P^\circ - P}{P^\circ} = X_{\text{solute}} = \frac{n}{n + N}$$

Simplifying this,

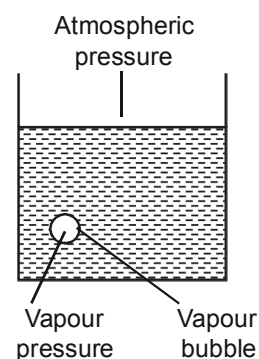
$$\frac{P^\circ - P}{P^\circ} = \frac{n}{N}$$

$$\therefore \frac{143 - 141.9}{141.9} = \frac{0.5/M}{154} \quad \text{or} \quad M = 62.86 \text{ g/mol}$$

ELEVATION IN BOILING POINT

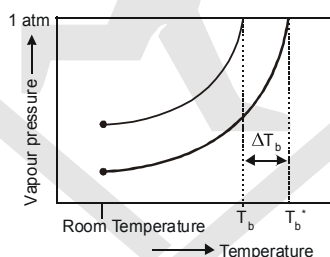
When a liquid boils, at a constant temperature the molecules of the liquid are converted into vapours, from any part of the liquid. It is different from evaporation because in evaporation the liquid converts to the vapour state only from the surface, while in boiling it does so from the bulk of the liquid also.

Consider the following figure in which a vapour of the liquid is formed in the bulk of the liquid. The vapour would exist as a vapour bubble in the liquid. This bubble experiences the atmospheric pressure on the outside while its vapour pressure is exerted inside.



Key concept:

The bubble will be formed only when the external pressure is slightly more (or almost equal to) the internal vapour pressure. Therefore, for the bulk of the liquid to form vapour, the vapour pressure must be equal to the external atmospheric pressure. Ignore the pressure of the liquid column above the bubble because it is negligible.



We can see from the figure that the solution needs to be heated to a higher temperature to make it boil. The difference between the boiling points of the solution and the solvent is known as the elevation in boiling point (ΔT_b).

Since $\Delta T_b \propto$ decrease in vapour pressure of solution \propto concentration of solute in the solution \propto molality of the solute in the solution,

$$\therefore \Delta T_b = K_b m$$

Where K_b is proportionality constant and is known as the molal boiling point elevation constant or the ebullioscopic constant. It has the units of degree kg mol⁻¹ or K kg mol⁻¹.

Significance of K_b

Now if, $m = 1$ then, $\Delta T_b = K_b$. Thus, the molal elevation constant is defined as the elevation of the boiling point when the molality of the solution is one i.e. when 1 mole of the solute is dissolved in 1 kg of the solvent, the elevation of boiling point is equal of K_b .

The values of molal elevation constant (K_b) for some common solvents are given in Table.

Molal elevation and molal freezing point constants

Solvent	Boiling point (K)	K_b (K kg mol ⁻¹)	Freezing point (K)	K_f (K kg mol ⁻¹)
Water	373.0	0.51	273.0	1.86
Ethyl alcohol	351.5	1.22	155.7	1.99
Benzene	353.3	2.53	278.6	5.12
Chloroform	334.4	3.63	209.6	4.68
Carbon tetrachloride	350.0	5.02	250.5	31.8
Carbon disulphide	319.4	2.34	164.2	3.83
Ether (C ₄ H ₁₀ O)	307.8	2.02	156.9	1.79
Camphor (C ₁₀ H ₁₆ O)	480.0	5.95	452.0	37.7

K_b and K_f can be obtained from the following relationships:

$$K_b = \frac{RT_b^2 M_{\text{solvent}}}{1000 \times \Delta_{\text{vap}} H} \quad \text{and} \quad K_f = \frac{RT_f^2 M_{\text{solvent}}}{1000 \times \Delta_{\text{fus}} H}$$

Where, T_b = boiling point of the solvent, T_f = freezing point of the solvent, M_{solvent} = molar mass of the solvent, $\Delta_{\text{vap}} H$ = enthalpy of vaporization and $\Delta_{\text{fus}} H$ = enthalpy of fusion.

Key concept:

Camphor is commonly used in determining the molecular mass of a solute because of its very high cryoscopic constant (K_f).

Illustration

A 5 percent aqueous solution by mass of a non-volatile solute boils at 100.15°C. Calculate the molar mass of the solute. $K_b = 0.52 \text{ K kg mol}^{-1}$.

Solution:

The normal boiling point of water is 100°C.

∴ The elevation in boiling point is 0.15°C.

A 5 percent solution means that in a 100 g solution 5 g of the solute is present. This implies that the solvent is 95 g.

If the molar mass of the solute is M , then the molality of the solute in the solution is,

$$\frac{5/M}{95} \times 1000, \quad \Delta T_b = K_b m$$

$$0.15 = 0.52 \times \frac{5/M}{95} \times 1000$$

$$\therefore M = 182.4 \text{ g/mol}$$

Illustration

Calculate the boiling point of a one molar aqueous solution (density: 1.03 g mL⁻¹) of sodium chloride. K_b for water = 0.52 K kg mol⁻¹; Atomic mass: Na = 23, Cl = 35.5.

Solution:

Conc. of the solution = 1 molar = 1 mol L⁻¹

Density of solution = 1.03 g mL⁻¹

Molar mass of NaCl = (23 + 35.5) g/mol = 58.5 g/mol

So, Mass of 1 litre of solution = 1000 × 1.03 = 1030 g

Therefore, Mass of water containing 1 mole of NaCl = (1030 – 58.5) g = 971.5g

Thus, Molality of the solution, $m = \frac{1 \times 1000}{971.5} \text{ mol/kg} = 1.0293 \text{ mol/kg}$

Then, $\Delta T_b = i \times K_b \times m = (2 \times 0.52 \times 1.0293) \text{ K} = 1.07 \text{ K}$

So, Boiling point of solution = (373.15 + 1.07) K = 374.22 K

Illustration

A solution of 12.5 g urea in 170 g of water gave a boiling point elevation of 0.63 K. Calculate the molar mass of urea, taking $K_b = 0.52 \text{ K/m}$.

Solution:

Given: Mass of urea, $w_2 = 12.5 \text{ g}$

Mass of water, $w_1 = 170 \text{ g} = 0.17 \text{ kg}$

Elevation of boiling point, $\Delta T_b = 0.63 \text{ K}$

Molar mass of urea, $M = ?$

$K_b = 0.52 \text{ K m}^{-1}$

Molar mass of the solute (urea) is given by:

$$M = \frac{K_b \times w_2}{w_1 \times \Delta T_b} = \frac{0.52 \times 12.5}{0.17 \times 0.63} \text{ g/mol} = 60.7 \text{ g mol}^{-1}$$

Illustration

Calculate the molecular mass of a substance 1.0 g of which on being dissolved in 100 g of solvent gave an elevation of 0.307 K in the boiling point. (Molal elevation constant (K_b) = 1.84 K/m).

Solution:

We know that, $\Delta T_b = \frac{K_b \times n_2}{w_1}$, where n_2 is the no. of moles of solute; w_1 is the mass of the solvent in kg.

$$n_2 = \frac{\text{Mass of solute}}{\text{Molar mass of the solute}} = \frac{1.0 \text{ g}}{M} \text{ and } w_1 = 100 \text{ g} = 0.1 \text{ kg}$$

Substituting these values, we get,

$$0.307 \text{ K} = \frac{1.84 \text{ K kg mol}^{-1}}{0.1 \text{ kg}} \times \frac{1.0 \text{ g}}{M}$$

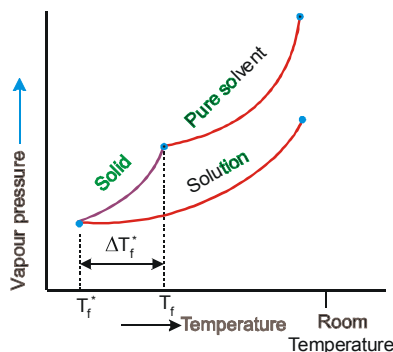
$$\text{So, } M = \frac{1.84 \text{ K kg mol}^{-1} \times 1.0 \text{ g}}{0.1 \text{ kg} \times 0.307 \text{ K}} = \frac{1.84 \times 1.0}{0.1 \times 0.307} \text{ g/mol} = 59.9 \text{ g/mol}$$

DEPRESSION IN FREEZING POINT

Freezing point of a substance is the temperature at which its liquid and the solid phases have the same vapour pressure.

Key concept:

As we already know from the definition of colligative properties that when a solution freezes, it is only the pure solvent which separated out in the solid form. It is this that causes a depression in the freezing point.



If the difference between the freezing point of the solvent and the solution is represented as ΔT_f , then $\Delta T_f = K_f m$, where, m = molality of the solution and K_f = molal freezing point depression constant or the cryoscopic constant. It has the units of degree kg mol^{-1} or K kg mol^{-1} .

Significance of K_f

$\Delta T_f = K_f m$. So, if $m = 1$ i.e. one mole of solute is dissolved in one kg of the solvent, then, $\Delta T_f = K_f$. Thus, the molal freezing point depression constant is equal to the depression in the freezing point produced when one mole of solute is dissolved in 1 kg of the solvent.

Illustration

An aqueous solution of a non-volatile solute boils at 100.17°C . At what temperature would it freeze? ($K_b = 0.52 \text{ K kg mol}^{-1}$ and $K_f = 1.86 \text{ K kg mol}^{-1}$).

Solution:

$$\Delta T_b = 0.17^\circ\text{C}$$

$$\therefore m = \frac{\Delta T_b}{K_b} = \frac{0.17}{0.52} = 0.327 \text{ molal, } \Delta T_f = K_f m$$

$$\Delta T_f = 1.86 \times 0.327 = 0.608$$

$$\therefore \text{Freezing point of the solution is } - 0.608^\circ\text{C}.$$

Illustration

Calculate the freezing point of a one-molar aqueous solution (density 1.06 g mL^{-1}) of KBr. K_f for water = $1.86 \text{ K kg mol}^{-1}$. Atomic mass: $\text{K} = 39$, $\text{Br} = 80$.

Solution:

$$\text{Mass of 1 litre of solution} = 1000 \text{ mL} \times 1.06 \text{ g mL}^{-1} = 1060 \text{ g}$$

$$\text{Molarity of solution} = 1 \text{ mol L}^{-1}$$

$$\text{Mass of KBr in 1 litre of solution} = (39 + 80) \text{ g} = 119 \text{ g}$$

$$\text{So, Mass of water containing 1 mole of KBr} = (1060 - 119) \text{ g} = 941 \text{ g}$$

$$\text{Molality of KBr solution} = \frac{1 \text{ mol}}{941 \text{ g}} \times 1000 \text{ g} = 1.0627 \text{ mol/kg}$$

Then, depression of freezing point (ΔT_f) is given by:

$$\Delta T_f = i K_f m = 2 \times 1.86 \times 1.0627 \text{ K} = 3.95 \text{ K}$$

$$\text{So, Freezing point of the solution} = (273.15 - 3.95) \text{ K} = 269.2 \text{ K}$$

Illustration

Ethylene glycol ($\text{HOH}_2\text{C} - \text{CH}_2\text{OH}$) is used as an antifreeze for water to be used in car radiators in cold places. How much ethylene glycol should be added to 1 kg of water to prevent it from freezing at -10°C ? Molal depression constant of water is $1.86 \text{ K kg mol}^{-1}$.

Solution:

Mass of water (solvent), $w_1 = 1 \text{ kg}$

$$\Delta T_f = 10^\circ\text{C}$$

$$K_f = 1.86 \text{ K kg mol}^{-1}$$

Mass of ethylene glycol required, $w_2 = ?$

Molar mass of ethylene glycol $= (12 + 3 + 16) \times 2 \text{ g/mol} = 62 \text{ g/mol}$

$$\text{We know, } \Delta T_f = \frac{K_f(w_2 / 62)}{w_1} \text{ or } 10 = \frac{1.86 \times w_2}{62 \times 1}$$

$$\text{This gives, } w_2 = \frac{10 \times 62 \times 1}{1.86} \text{ g} = 333.3 \text{ g}$$

Illustration

Normal freezing point of a solvent is 150°C . A 0.5 molal solution of urea in the above solvent causes a freezing point depression of two degrees. Calculate the molal depression constant

Solution:

We know, $\Delta T_f = K_f m$

$$\text{So, } K_f = \frac{\Delta T_f}{m} = \frac{2 \text{ deg}}{0.5 \text{ mol kg}^{-1}} = 4 \text{ deg. kg mol}^{-1}$$

Illustration : A solution of urea in water freezes at 0.400°C . What will be the boiling point of the same solution if the depression and elevation constants for water are $1.86 \text{ deg kg mol}^{-1}$ and $0.512 \text{ deg kg mol}^{-1}$ respectively?

Solution: We have the relationships:

$$\Delta T_b = \frac{K_b n_2}{w_1} \quad \dots(i)$$

$$\text{And } \Delta T_f = \frac{K_f n_2}{w_1} \quad \dots(ii)$$

Where, n_2 is the number of moles of the solute, and w_1 is the mass of solvent in kg.

Dividing equation (i) by equation (ii),

$$\frac{\Delta T_b}{\Delta T_f} = \frac{K_b}{K_f}$$

$$\text{or, } \Delta T_b = \frac{\Delta T_f \times K_b}{K_f} = \frac{0.4 \times 0.512}{1.86} ^\circ\text{C} = 0.11^\circ\text{C}$$

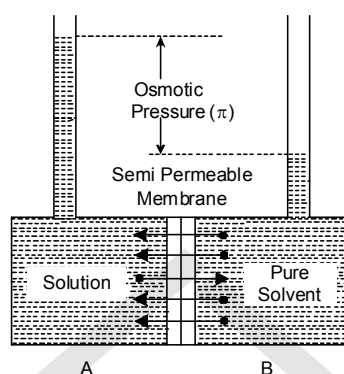
Then, Boiling point of the urea solution $= 100^\circ\text{C} + 0.11^\circ\text{C} = 100.11^\circ\text{C}$

CONCEPT OF OSMOTIC PRESSURE

In the process of Osmosis, solvent moves from a region of its higher concentration to a region of its lower concentration through a semi-permeable membrane, which allows the free passage of only solvent molecules. The extra pressure developed on the solution side as a result of the solvent flow is called osmotic pressure (π). It can also be defined as: *the minimum pressure which should be applied on the solution, so as to prevent the migration of solvent molecules into the solution through a semi-permeable membrane*. Some typical examples of osmosis and osmotic pressure are:

- (i) The climbing of water up a tall tree from the soil.
- (ii) Bursting of red-blood cells when placed in water.
- (ii) Swelling of dry raisings when placed in water.

Key concept: *The semipermeable membranes allow a selective passage to only the solvent molecules. Cellophane, parchment paper and animal protein membranes are typical semipermeable membranes.*



The Van't Hoff equation describes the relationship between the osmotic pressure and concentration

of solute in the solution. $\pi = \frac{n}{V} RT = cRT$, where n is the no. of moles of solute in the solution and V is the volume of the solution.

Difference between Osmotic Pressure and Vapour Pressure

Osmotic pressure	Vapour pressure
It is the minimum pressure which should be applied on the solution so as to prevent the migration of solvent molecules into the solution through a semi-permeable membrane.	It is the maximum pressure exerted by the vapour above the surface of solution in a closed container.

Illustration

Calculate the osmotic pressure and vapour pressure of 0.6% aqueous solution of a non-volatile, non-electrolyte solute, urea (NH_2CONH_2) at 25°C . The vapour pressure of pure water at 25°C is 24 mm Hg. Take densities to be 1 g mL^{-1} and assume ideal behaviour of the solution. Gas constant, $R = 0.082 \text{ L atm. mol}^{-1} \text{ K}^{-1}$.

Key concept:

Please refer to difference between osmotic pressure and vapour pressure while solving this illustration.

Solution:

Concentration of urea solution = 0.6%

This means, solution contains 0.6 g of urea per 100 g, and hence 100 mL of the solution,

So,

$$\text{Mass of urea per litre of solution} = \frac{0.6}{100} \times 100 = 6 \text{ g}$$

Molar mass of urea, $M = 60 \text{ g/mol}$

$$\text{Concentration of urea in solution} = \frac{6}{60} \text{ mol/L} = 0.1 \text{ mol/L}$$

Illustration

At 25°C , the osmotic pressure of human blood due to the pressure of various solutes in the blood is 7.65 atm . Assuming that molarity and molality are almost same, calculate the freezing point of blood. $K_f = 1.86 \text{ K kg/mol}$.

Solution:

According to the Van't Hoff equation,

$$\pi = cRT$$

$$c = \frac{7.65}{(0.082)(298)} = 0.313 \text{ mol/L}$$

Since molarity and molality are same,

$$\Delta T_f = K_f m$$

$$\Delta T_f = 1.86 \times 0.313 = 0.582$$

\therefore Freezing point of blood is -0.582°C .

VAN'T HOFF FACTOR

Several solutes have a tendency to dissociate or associate when dissolved in a solvent. Since the colligative properties are directly proportional to the no. of mole of the solute, dissociation or association may cause some abnormal increase or decrease in the measured values of colligative properties. Van't Hoff factor is a factor that takes into account this abnormal behaviour and can be defined as,

$$i = \frac{\text{Observed magnitude of any colligative property}}{\text{Normal magnitude of the same colligative property}}$$

Since, colligative properties are inversely related to the molar mass of the solute, hence, one can write,

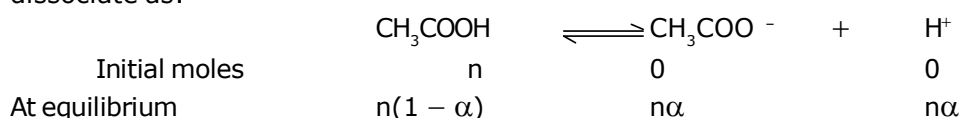
$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass (obtained from a colligative property)}}$$

Thus, the value of i depends upon the state of solute in the solution. Following cases become possible.

1. When, $i = 1$, then the solute remains unaffected (i.e., normal) in solution.
2. When, $i > 1$, then the solute undergo dissociation in solution.
3. When, $i < 1$, then the solute undergo association in solution.

Thus, for	Potassium chloride (KCl)	in aqueous solution, i is nearly equal to 2.
	Barium chloride (BaCl_2)	in aqueous solution, i is nearly equal to 3.
	Benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$)	in benzene, i is nearly equal to 0.5.
	Acetic acid (CH_3COOH)	in benzene, i is nearly equal to 0.5.

Let us take for example the dissolution of acetic acid in water. When dissolved, acetic acid would dissociate as:



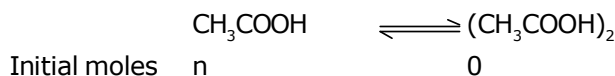
Total number of moles at equilibrium = $n - n\alpha + n\alpha + n\alpha = n(1 + \alpha)$

Van't Hoff factor is defined as the ratio of the no. of moles after dissolution to the no. of moles before dissolution.

$$\therefore \frac{n(1 + \alpha)}{n} = i = \text{Van't Hoff factor}$$

$$\therefore i = 1 + \alpha$$

When acetic acid is dissolved in benzene, it associates as:



$$\text{At equilibrium } n(1 - \alpha) \qquad \frac{n\alpha}{2}$$

$$\therefore i = \frac{n\left(1 - \frac{\alpha}{2}\right)}{n} = 1 - \frac{\alpha}{2}$$

Therefore when a solute dissociates, i will be more than 1 and when it associates, i will be less than 1, when it does neither, i is equal 1.

A colligative property is a property which is such that,

$$\frac{\text{Actual colligative property}}{\text{Theoretical colligative property}} = i$$

Where actual colligative property is the value that is calculated experimentally and the theoretical colligative property is the value that is calculated based on the no. of moles of solute added.

Key concept:

Among all the colligative properties that we have studied so far, relative lowering of vapour pressure does not satisfy the equation given above. It would do so if the solution were very dilute so that we ignore n in the denominator.

$$\therefore \frac{P^\circ - P}{P^\circ} = \frac{n}{n + N} \approx \frac{n}{N}. \text{ In fact it would be convenient to use the expression } \frac{P^\circ - P}{P^\circ} \text{ in numerical}$$

problems which is equal to $\frac{n}{N}$ rather than $\frac{P^\circ - P}{P^\circ}$.

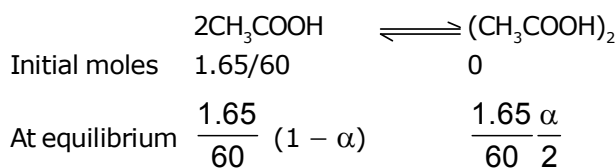
Modified Equations for Colligative Properties

For solutes which undergo dissociation or association in solutions, the equations for the colligative properties are modified by inserting the van't-Hoff's factor in them as follows:

Colligative property	equation for colligative property	
	when solute remains normal	when the solute undergoes association/dissociation
1. Relative lowering of vapour pressure	$\frac{p_s^\circ - p_s}{p_s^\circ} = X_{\text{solute}}$	$\frac{p_s^\circ - p_s}{p_s^\circ} = i X_{\text{solute}}$
2. Elevation of the boiling point	$\Delta T_b = K_b \times m$	$\Delta T_b = i K_b \times m$
3. Depression of the freezing point	$\Delta T_f = K_f \times m$	$\Delta T_f = i K_f \times m$
4. Osmotic pressure	$\pi = CRT$	$\pi = i CRT$

Illustration

Acetic acid (CH_3COOH) associates in benzene to form double molecules. 1.65 g of acetic acid when dissolved in 100 g of benzene raised the boiling point by 0.36°C . Calculate the Van't Hoff factor and the degree of association of acetic acid in benzene. ($K_b = 2.57 \text{ K kg mol}^{-1}$).

Solution:

$$\text{Total moles at equilibrium} = \frac{1.65}{60} \left(1 - \frac{\alpha}{2}\right)$$

$$\Delta T_b = K_b \times m, \quad 0.36 = 2.57 \times \frac{1.65}{60} \left(1 - \frac{\alpha}{2}\right)$$

$$\alpha = 0.981$$

$$\text{Van't Hoff factor} = \frac{\text{no. of moles at equilibrium}}{\text{Initial no. of moles}} = i$$

$$i = 1 - \frac{\alpha}{2} = 0.5$$

Illustration : Derive a relationship between K_p , T_b and ΔH_{vap} for a liquid.**Solution:**

Let us consider a pure liquid. At its boiling point, T_b , its vapour pressure P° would be equal to the external pressure.

$$\therefore P^\circ = P_{\text{ext}} \text{ at temperature } T_b.$$

Now let us consider a non-volatile solute dissolved in the liquid. When the solution reaches temperature T_b , the vapour pressure of the system, would be less than the external pressure. When the solution is heated further and it reaches its boiling T_b^* , the vapour pressure of the solution would be equal to P_{ext} which is equal to the P° of the pure liquid at its boiling point. Since vapour pressure of a system are the K_p 's for the respective equilibrium,

$$\ln \frac{K_{PT_2}}{K_{PT_1}} = \frac{\Delta H}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\ln \frac{P^\circ}{P} = \frac{\Delta H_{\text{vap}}}{R} \left[\frac{1}{T_b} - \frac{1}{T_b^*} \right] = \frac{\Delta H_{\text{vap}}}{R} \left[\frac{\Delta T_b}{T_b T_b^*} \right]$$

Assuming the solution to be highly dilute, T_b^* would be very close to T_b .

$$\therefore \ln \frac{P^\circ}{P} = \frac{\Delta H_{\text{vap}}}{R} \left[\frac{\Delta T_b}{T_b^2} \right]$$

$$-\ln \frac{P}{P^\circ} = \frac{\Delta H_{\text{vap}}}{R} \left[\frac{\Delta T_b}{T_b^2} \right]$$

$$-\ln \left[1 - \left(\frac{P^\circ - P}{P^\circ} \right) \right] = \frac{\Delta H_{\text{vap}}}{R} \left[\frac{\Delta T_b}{T_b^2} \right]$$

$$-\ln[1 - X_{\text{solute}}] = \frac{\Delta H_{\text{vap}}}{R} \left[\frac{\Delta T_b}{T_b^2} \right]$$

Since X_{solute} is very small, we can make the approximation that $\ln(1 - x) = -x$ (when x is very small).

$$\therefore X_{\text{solute}} = \frac{\Delta H_{\text{vap}}}{R} \left[\frac{\Delta T_b}{T_b^2} \right] \quad \text{or} \quad \frac{n}{n+N} = \frac{\Delta H_{\text{vap}}}{R} \left[\frac{\Delta T_b}{T_b^2} \right]$$

Ignoring n in comparison to N in the denominator

$$\frac{n}{N} = \frac{\Delta H_{\text{vap}}}{R} \left[\frac{\Delta T_b}{T_b^2} \right]$$

$$\frac{\frac{n}{W_{\text{solvent}}}}{\frac{M_{\text{solvent}}}{1000}} = \frac{\Delta H_{\text{vap}}}{R} \left[\frac{\Delta T_b}{T_b^2} \right] \quad \text{or} \quad \frac{n}{W_{\text{solvent}}} = \frac{\Delta H_{\text{vap}}}{M_{\text{solvent}} R} \left[\frac{\Delta T_b}{T_b^2} \right]$$

Multiplying by 1000 on both the sides, we get,

$$\frac{n}{W_{\text{solvent}}} \times 1000 = \frac{\Delta H_{\text{vap}}}{M_{\text{solvent}} R} \left[\frac{\Delta T_b}{T_b^2} \right] \times 1000$$

$$m = \frac{\Delta H_{\text{vap}}}{M_{\text{solvent}} R} \left[\frac{K_b m}{T_b^2} \right] \times 1000$$

$$\therefore K_b = \frac{RT_b^2 M_{\text{solvent}}}{1000 \Delta H_{\text{vap}}}$$

$$\text{Similarly, } K_f = \frac{RT_b^2 M_{\text{solvent}}}{1000 \Delta H_{\text{fus}}}$$

Illustration : To 500 cm³ of water, 3.0 × 10⁻³ kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point? K_f and density of water are 1.86 K kg⁻¹ mol⁻¹ and 0.997 g cm⁻³ respectively.

Solution: Molality of acetic acid = $\frac{3 \times 10^{-3} \times 10^3 \times 1000}{60 \times 0.997 \times 500} = 0.1003$

Total number of moles per kg of solvent = 0.1003 (1 + 0.23)

$$\Delta T_f = K_f m = 1.86 \times 0.1003 \times 1.23 = 0.23^\circ\text{C}$$

Illustration : At 300 K, the vapour pressure of an ideal solution containing one mole of A and 3 moles of B is 500 mm of Hg. At the same temperature, if one mole of B is added to this solution, the vapour pressure of the solution increases by 10 mm of Hg. Calculate the V.P. of A and B in their pure state.

Solution: Initially, $P_M = P_A^\circ X_A + P_B^\circ X_B$

$$550 = P_A^\circ \frac{1}{1+3} + P_B^\circ \frac{3}{1+3} \quad \text{or} \quad P_A^\circ + 3P_B^\circ = 2200 \quad \dots(i)$$

When, one mole of B is further added to it, $P_M = P_A^\circ X_A + P_B^\circ X_B$

$$56. = P_A^\circ \frac{1}{1+4} + P_B^\circ \frac{4}{1+4} \quad \therefore \quad P_A^\circ + 4P_B^\circ = 2800 \quad \dots(ii)$$

Solving equations (i) and (ii), we get

$$P_A^\circ = 440 \text{ mm}, P_B^\circ = 600 \text{ mm}$$

Illustration : A decinormal solution of NaCl exerts an osmotic pressure of 4.6 atm. at 300 K. Calculate its degree of dissociation. ($R = 0.082 \text{ L atm. K}^{-1} \text{ mol}^{-1}$).

Solution: No. of moles of NaCl per litre of solution = 0.1

Osmotic pressure (π) = 4.6 atm., Temperature (T) = 300 K

Had NaCl not dissociated, then

$$\pi_{\text{normal}} = CRT = 0.1 \times 0.082 \times 300 \text{ atm.} = 2.46 \text{ atm.}$$

But, $\pi_{\text{obs}} = 4.6 \text{ atm.}$

As per definition,

$$i = \frac{\text{Observed magnitude of a colligative property}}{\text{Normal magnitude of a colligative property}} = \frac{\pi_{\text{obs}}}{\pi_{\text{normal}}} = \frac{4.6 \text{ atm.}}{2.46 \text{ atm.}} = 1.87$$

For the dissociation of an electrolyte producing n ions,

$$\alpha = \frac{i-1}{n-1} = \frac{1.87-1}{2-1} = \frac{0.87}{1} = 0.87$$

So, Percentage dissociation = $100 \times \alpha = 100 \times 0.87 = 87\%$

Illustration : Vapour pressure of C_6H_6 and C_7H_8 mixture at 50°C are given by:

$P = 179 X_B + 92$, where X_B is mole fraction of C_6H_6 . Calculate (in mm):

(A) Vapour pressure of pure liquids.

(B) Vapour pressure of liquid mixture obtained by mixing 936 g C_6H_6 and 736 g toluene.

(C) If the vapours are removed and condensed into liquid and again brought to the temperature of 50°C , what would be mole fraction of C_6H_6 in vapour state?

Solution: (A) Given, $P = 179X_B + 92$

For pure, C_6H_6 , $X_B = 1$

$$\therefore P_B^\circ = 179 + 92 = 271 \text{ mm}$$

For pure C_7H_8 , $X_B = 0$

$$\therefore P_T^\circ = 179 \times 0 + 92 = 92 \text{ mm}$$

(B) Now $P_M = P_B^\circ X_B + P_T^\circ X_T$

$$= 271 \times \frac{12}{12+8} + 92 \times \frac{8}{12+8} = 162.6 + 36.8 = 199.4 \text{ mm}$$

$$\text{Moles of } C_6H_6 = \frac{936}{78} = 12$$

$$\text{Moles of } C_7H_8 = \frac{736}{92} = 8$$

(C) Now mole fraction of C_6H_6 in vapour phase of initial mixture (X_T')

$$X_T' = \frac{P_B'}{P_M} = \frac{162.6}{199.4} = 0.815$$

Moles fraction of C_7H_8 in vapour phase of initial mixture (X_T')

$$X_T' = \frac{P_T'}{P_M} = \frac{36.8}{199.4} = 0.185$$

These vapours are taken out and condensed into liquid. The liquid is again brought to 50°C to get again vapour-liquid equilibrium.

Thus, mole fraction of C_6H_6 in vapour phase of initial mixture

$$= \text{Mole fraction of } C_6H_6 \text{ in liquid phase on II mixture } X_B'$$

Similarly, mole fraction of C_7H_8 in vapour phase of initial mixture

$$= \text{Mole fraction of } C_7H_8 \text{ in liquid phase on II mixture } X_T'$$

$$\text{New } P_M = P_B' + P_T'$$

$$\text{Therefore, new } P_M = P_B^\circ X_B' + P_T^\circ X_T'$$

$$= 271 \times 0.815 + 92 \times 0.185 \text{ mm}$$

$$= 220.865 + 17.02 = 237.885 \text{ mm}$$

$$\therefore \text{ New mole fraction of } C_6H_6 \text{ in vapour phase} = \frac{\text{New } P_B'}{\text{New } P_M} = \frac{220.865}{237.885}$$

$$= 0.928$$

$$\therefore \text{ New mole fraction of } C_7H_8 \text{ in vapour phase} = 0.072$$

SOLVED EXAMPLE

Ex.1 The molarity of 20% (W/W) solution of sulphuric acid is 2.55 M. The density of the solution is :

- (A) 1.25 g cm^{-3} (B) 0.125 g L^{-1} (C) 2.55 g cm^{-3} (D) unpredictable
(Ans. A)

Sol. Volume of 100 g of solution = $\frac{100}{d}$ ml

$$\therefore M = \frac{20 \times d \times 1000}{100 \times 98}$$

$$\text{or } d = \frac{2.55 \times 100 \times 98}{20 \times 1000} = 1.249 \approx 1.25$$

Ex.2 The density of a solution containing 13% by mass of sulphuric acid is 1.09 g/mL. Calculate the molarity and normality of the solution-

- (A) 1.445 M (B) 14.45 M (C) 144.5 M (D) 0.1445 M
(Ans. A)

Sol. Volume of 100 gram of the solution = $\frac{100}{d}$

$$= \frac{100}{1.09} \text{ mL} = \frac{100}{1.09 \times 1000} \text{ litre}$$

$$= \frac{1}{1.09 \times 10} \text{ litre}$$

$$\text{Number of moles of } \text{H}_2\text{SO}_4 \text{ in 100 gram of the solution} = \frac{13}{98}$$

$$\text{Molarity} = \frac{\text{No. of moles of } \text{H}_2\text{SO}_4}{\text{Volume of solution in litre}}$$

$$= \frac{13}{98} \times \frac{1.09 \times 10}{1} = \mathbf{1.445 \text{ M}}$$

Ex.3 Calculate the molarity of pure water ($d = 1 \text{ g/L}$)

- (A) 555 M (B) 5.55 M (C) 55.5 M (D) None **(Ans. C)**

Sol. Consider 1000 mL of water

Mass of 1000 mL of water

$$= 1000 \times 1 = 1000 \text{ gram}$$

$$\text{Number of moles of water} = \frac{1000}{18} = 55.5$$

$$\text{Molarity} = \frac{\text{No. of moles of water}}{\text{Volume in litre}}$$

$$= \frac{55.5}{1} = \mathbf{55.5\ M}$$

Ex.4 Calculate the quantity of sodium carbonate (anhydrous) required to prepare 250 ml of 0.1 M solution-

- (A) 2.65 gram (B) 4.95 gram (C) 6.25 gram (D) None **(Ans. A)**

Sol. We know that

$$\text{Molarity} = \frac{W}{M \times V}$$

where;

W = Mass of Na_2CO_3 in gram

M = Molecular mass of Na_2CO_3 in grams = 106

$$V = \text{Volume of solution in litres} = \frac{250}{1000} = 0.25$$

$$\text{Molarity} = \frac{1}{10}$$

$$\text{Hence, } \frac{1}{10} = \frac{W}{106 \times 0.25}$$

$$\text{or } W = \frac{106 \times 0.25}{10} = \mathbf{2.65\ gram}$$

Ex.5 The freezing point of a 0.08 molal aqueous solution of NaHSO_4 is -0.372°C . The dissociation constant for the reaction



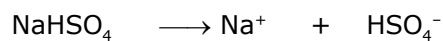
- (A) 4×10^{-2} (B) 8×10^{-2} (C) 2×10^{-2} (D) 1.86×10^{-2}

(Ans. A)

Sol. $\Delta T_f = K_f \times m$

$$m = \frac{\Delta T_f}{K_f} = \frac{0.372}{1.86} = 0.2$$

This means that total molal conc. of all particles is 0.2.



$$0.08 \qquad \qquad \qquad 0.08$$



$$(0.08 - x) \qquad x \qquad x$$

The net particle concentration

$$0.087 = (0.08 - x) + x + x = 0.2$$

$$\text{or } x = 0.04$$

$$K_a = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = 0.04$$

- Ex.6** Find the molality of H_2SO_4 solution whose specific gravity is 1.98 g ml^{-1} and 95% by volume H_2SO_4
 (A) 7.412 (B) 8.412 (C) 9.412 (D) 10.412 **(Ans. C)**

Sol. H_2SO_4 is 95% by volume
 wt. of H_2SO_4 = 95g
 Vol of solution = 100ml

$$\therefore \text{Moles of } H_2SO_4 = \frac{95}{98}, \text{ and weight of solution} = 100 \times 1.98 = 198 \text{ g}$$

$$\text{Weight of water} = 198 - 95 = 103 \text{ g}$$

$$\text{Molality} = \frac{95 \times 1000}{98 \times 103} = 9.412$$

Hence molality of H_2SO_4 solution is **9.412**

- Ex.7** Calculate molality of 1 litre solution of 93% H_2SO_4 by volume. The density of solution is 1.84 gm ml^{-1}
 (A) 9.42 (B) 10.42 (C) 11.42 (D) 12.42 **(Ans. B)**

Sol. Given H_2SO_4 is 93% by volume

$$\text{wt. of } H_2SO_4 = 93\text{g}$$

$$\text{Volume of solution} = 100\text{ml}$$

$$\therefore \text{weight of solution} = 100 \times 1.84 \text{ gm} \\ = 184 \text{ gm}$$

$$\text{wt. of water} = 184 - 93 = 91 \text{ gm}$$

$$\text{Molality} = \frac{\text{Moles}}{\text{wt. of water in kg}}$$

$$= \frac{93 \times 1000}{98 \times 91} = 10.42$$

- Ex.8** Suppose 5gm of CH_3COOH is dissolved in one litre of Ethanol. Assume no reaction between them. Calculate molality of resulting solution if density of Ethanol is 0.789 gm/ml .
 (A) 0.0856 (B) 0.0956 (C) 0.1056 (D) 0.1156 **(Ans. C)**

Sol. Wt. of CH_3COOH dissolved = 5g

$$\text{Eq. of } CH_3COOH \text{ dissolved} = \frac{5}{60}$$

$$\text{Volume of ethanol} = 1 \text{ litre} = 1000\text{ml.}$$

$$\therefore \text{Weight of ethanol} = 1000 \times 0.789 = 789\text{g}$$

$$\therefore \text{Molality of solution} = \frac{\text{Moles of solute}}{\text{wt of solvent in kg}}$$

$$= \frac{5}{\frac{60 \times 789}{1000}} = 0.1056$$

Ex.9 Calculate the molarity and normality of a solution containing 0.5 gm of NaOH dissolved in 500 ml. solution-

(A) 0.0025 M, 0.025 N

(B) 0.025 M, 0.025 N

(C) 0.25 M, 0.25 N

(D) 0.025 M, 0.0025 N

(Ans. B)

Sol. Wt. of NaOH dissolved = 0.5 gm

Vol. of NaOH solution = 500 ml

Calculation of molarity

$$0.5 \text{ g of NaOH} = \frac{0.5}{40} \text{ moles of NaOH}$$

[\because Mol. wt of NaOH = 40]

$$= 0.0125 \text{ moles}$$

Thus 500 ml of the solution contain NaOH = 0.0125 moles

\therefore 1000 ml of the solution contain

$$= \frac{0.0125}{500} \times 1000$$

$$= 0.025 \text{ M}$$

Hence molarity of the solution = **0.025 M**

Calculation of normality

Since NaOH is monoacidic ;

Eq. wt. of NaOH = Mol. wt. of NaOH = 40

$$\therefore 0.5 \text{ gm of NaOH} = \frac{0.5}{40} \text{ gm equivalents} = 0.0125 \text{ gm equivalents}$$

Thus 500 ml of the solution contain NaOH = 0.0125 gm equ.

\therefore 1000 ml of the solution contain

$$= \frac{0.0125}{500} \times 1000 = 0.025$$

Hence normality of the solution = **0.025 N**

Ex.10 Calculate the molality and mole fraction of the solute in aqueous solution containing 3.0 gm of urea per 250 gm of water (Mol. wt. of urea = 60).

(A) 0.2 m, 0.00357

(B) 0.4 m, 0.00357

(C) 0.5 m, 0.00357

(D) 0.7m, 0.00357

(Ans. A)

Sol. Wt. of solute (urea) dissolved = 3.0 gm

Wt. of the solvent (water) = 250 gm

Mol. wt. of the solute = 60

$$3.0 \text{ gm of the solute} = \frac{3.0}{60} \text{ moles} = 0.05 \text{ moles}$$

Thus 250 gm of the solvent contain = 0.05 moles of solute

$$\therefore 1000 \text{ gm of the solvent contain} = \frac{0.05 \times 1000}{250} = 0.2 \text{ moles}$$

Hence molality of the solution = 0.2 m

In short,

Molality = No. of moles of solute/1000 g of solvent

$$\therefore \text{Molality} = \frac{3/60}{250} \times 1000 = \mathbf{0.2 \text{ m}}$$

Calculation of mole fraction

3.0 gm of solute = $3/60$ moles = 0.05 moles

$$250 \text{ gm of water} = \frac{250}{18} \text{ moles}$$

$$= 13.94 \text{ moles}$$

\therefore Mole fraction of the solute

$$= \frac{0.05}{0.05 + 13.94} = \frac{0.05}{13.99}$$

$$= \mathbf{0.00357}$$

Ex.11 A solution has 25% of water, 25% ethanol and 50% acetic acid by mass. Calculate the mole fraction of each component.

(A) 0.50, 0.3, 0.19 (B) 0.19, 0.3, 0.50 (C) 0.3, 0.19, 0.50 (D) 0.50, 0.19, 0.3

(Ans. D)

Sol. Since 18 g of water = 1 mole

$$25 \text{ g of water} = \frac{25}{18} = 1.38 \text{ mole}$$

Similarly, 46 g of ethanol = 1 mole

$$25 \text{ g of ethanol} = \frac{25}{46} = 0.55 \text{ moles}$$

Again, 60 g of acetic acid = 1 mole

$$50 \text{ g of acetic acid} = \frac{50}{60} = 0.83 \text{ mole}$$

\therefore Mole fraction of water

$$= \frac{1.38}{1.38 + 0.55 + 0.83} = \mathbf{0.50}$$

Similarly, Mole fraction of ethanol

$$= \frac{0.55}{1.38 + 0.55 + 0.83} = \mathbf{0.19}$$

Mole fraction of acetic acid

$$= \frac{0.83}{1.38 + 0.55 + 0.83} = \mathbf{0.3}$$

Ex.12 15 gram of methyl alcohol is dissolved in 35 gram of water. What is the mass percentage of methyl alcohol in solution ?

- (A) 30% (B) 50% (C) 70% (D) 75% **(Ans. A)**

Sol. Total mass of solution = (15 + 35) gram = 50 gram
mass percentage of methyl alcohol

$$= \frac{\text{Mass of methyl alcohol}}{\text{Mass of solution}} \times 100$$

$$= \frac{15}{50} \times 100 = \mathbf{30\%}$$

Ex.13 Calculate the masses of cane sugar and water required to prepare 250 gram of 25% cane sugar solution-

- (A) 187.5 gram, 62.5 gram (B) 62.5 gram, 187.5 gram
(C) 162.5 gram, 87.5 gram (D) None of these **(Ans. B)**

Sol. Mass percentage of sugar = 25
We know that

$$\text{Mass percentage} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

$$\text{So, } 25 = \frac{\text{Mass of cane sugar}}{250} \times 100$$

$$\text{or Mass of cane sugar} = \frac{25 \times 250}{100}$$

$$= \mathbf{62.5 \text{ gram}}$$

$$\text{Mass of water} = (250 - 62.5) = \mathbf{187.5 \text{ gram}}$$

Ex.14 Calculate normality of the mixture obtained by mixing 100ml of 0.1N HCl and 50ml of 0.25N NaOH solution.

- (A) 0.0467 N (B) 0.0367 N (C) 0.0267 N (D) 0.0167 N **(Ans. D)**

Sol. Meq. of HCl = $100 \times 0.1 = 10$

$$\text{Meq. of NaOH} = 50 \times 0.25 = 12.5$$

\therefore HCl and NaOH neutralize each other with equal eq.

$$\text{Meq. of NaOH left} = 12.5 - 10 = 2.5$$

$$\text{Volume of new solution} = 100 + 50 = 150 \text{ ml.}$$

$$N_{\text{NaOH left}} = \frac{2.5}{150} = 0.0167 \text{ N}$$

Hence normality of the mixture obtained is **0.0167 N**

Ex.15 300 ml 0.1 M HCl and 200 ml of 0.03M H₂SO₄ are mixed. Calculate the normality of the resulting mixture-

- (A) 0.084 N (B) 0.84 N (C) 2.04 N (D) 2.84 N **(Ans.A)**

Sol. For HCl
 $V_1 = 300 \text{ ml}$
 $N_1 = M \times \text{Basicity}$
 $= 0.1 \times 1 = 0.1$

For H_2SO_4
 $V_2 = 200 \text{ ml}$
 $N_2 = M \times \text{Basicity}$
 $= 0.03 \times 2 = 0.06$

Normality of the mixture,

$$N = \frac{V_1 N_1 + V_2 N_2}{V_1 + V_2}$$

$$= \frac{300 \times 0.1 + 200 \times 0.06}{500}$$

$$= \frac{30 + 12}{500} = \mathbf{0.084 \text{ N}}$$

Ex.16 In what ratio should a 6.5 N HNO_3 be diluted with water to get 3.5 N HNO_3 ?

- (A) 6 : 7 (B) 7 : 6 (C) 5 : 6 (D) 6 : 5 **(Ans. B)**

Sol. $N_1 V_1 = N_2 V_2$
 $6.5 V_1 = 3.5 (V_1 + x)$
 $6.5 V_1 = 3.5 V_1 + 3.5 x$
 $3 V_1 = 3.5 x$
 $\frac{V_1}{x} = \frac{3.5}{3} = \frac{7}{6}$

Ex.17 Calculate the amount of each in the following solutions -

- (i) 150 ml of $\frac{N}{7} \text{ H}_2\text{SO}_4$ (ii) 250 ml of 0.2M NaHCO_3
- (iii) 400 ml of $\frac{N}{10} \text{ Na}_2\text{CO}_3$ (iv) 1052 g of 1 m KOH.
- (A) 52g, 2.12g, 4.2g, 1.05g (B) 1.05g, 4.2g, 2.12g, 52g
- (C) 1.05g, 2.12g, 52g, 4.2g (D) 4.2g, 2.12g, 1.05g, 52g **(Ans. B)**

Sol. (i) Eq. wt. of $\text{H}_2\text{SO}_4 = \frac{\text{Mol. wt}}{\text{Basicity}} = \frac{98}{2} = 49$

\therefore Amount of H_2SO_4 per litre (strength) = Normality \times Eq. wt. = $\frac{1}{7} \times 49 = 7 \text{ g/litre}$

Amount in 150 ml = $\frac{7 \times 150}{1000} = 1.05 \text{ g}$

(ii) Molecular wt. of

$$\text{NaHCO}_3 = 23 + 1 + 12 + 48 = 84$$

Amount of NaHCO_3 required to produce 1000 c.c. of one molar solution = 84 g

Amount present per litre in 0.2 M solution = $84 \times 0.2 = 16.8 \text{ g}$

\therefore Amount present in 250 c.c.

$$= \frac{16.8 \times 250}{1000} = 4.2 \text{ g}$$

(iii) Equivalent weight of

$$\text{Na}_2\text{CO}_3 = \frac{\text{Mol.wt}}{\text{No. of positive valencies}}$$

$$= \frac{106}{2} = 53$$

$$\text{Amount of Na}_2\text{CO}_3 = \text{Normality} \times \text{Eq. wt.} = \frac{1}{10} \times 53 = 5.3 \text{ g/litre}$$

$$\therefore \text{Amount present in 400 c.c.} = \frac{5.3 \times 400}{1000} = 2.12 \text{ g}$$

(iv) We know that 1 molal solution of a substance contains 1000 g of solvent.

$$\therefore \text{Wt. of KOH in 1052 g of 1 m KOH solution} = 1052 - 1000 = 52 \text{ g}$$

Ex.18 How many kilograms of wet NaOH containing 12% water are required to prepare 60 litres of 0.50 N solution ?

- (A) 1.36 kg (B) 1.50 kg (C) 2.40 gm (D) 3.16 kg **(Ans. A)**

Sol. One litre of 0.50 N NaOH contains = $0.50 \times 40\text{g} = 20 \text{ g} = 0.020 \text{ kg}$

\therefore 60 litres of 0.50 N NaOH contain

$$= 0.020 \times 60 \text{ kg} = 1.20 \text{ kg NaOH}$$

Since the given NaOH contains 12% water, the amount of pure NaOH in 100 kg of the given NaOH = $100 - 12 = 88 \text{ kg}$

Thus 88 kg of pure NaOH is present in 100 kg wet NaOH

\therefore 1.20 kg of pure NaOH is present in

$$= \frac{100}{88} \times 1.20 = \mathbf{1.36 \text{ kg wet NaOH}}$$

Ex. 19 Calculate the vapour pressure of a solution at 100°C containing 3g of cane sugar in 33g of water. (At wt. C = 12, H = 1, O = 16)

- (A) 760 mm (B) 756.90 mm (C) 758.30 mm (D) None **(Ans. B)**

Sol. Vapour pressure of pure water (solvent) at 100°C , $p^0 = 760 \text{ mm}$.

Vapour pressure of solution, $p = ?$

Wt. of solvent, $W = 33\text{g}$

Wt. of solute, $w = 3\text{g}$

Mol. wt. of water (H_2O), $M = 18$

Mol. wt. of sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$),

$$m = 12 \times 12 + 22 \times 1 + 11 \times 16 = 342$$

According to Raoult's law ,

$$\frac{p^0 - p}{p^0} = \frac{wM}{Wm}$$

$$\therefore p = p^0 - \frac{w \times M}{m \times W} \times p^0$$

$$p = 760 - \frac{3 \times 18}{342 \times 33} \times 760$$

$$(\because p^0 \text{ for } H_2O = 760 \text{ mm})$$

$$= 760 - 3.19 = 756.90 \text{ mm}$$

Ex.20 Osmotic pressure of a sugar solution at 24°C is 2.5 atmospheres. Determine the concentration of the solution in gm mole per litre.

(A) 0.0821 moles/litre

(B) 1.082 moles/litre

(C) 0.1025 moles/litre

(D) 0.0827 moles/litre

(Ans. C)

Sol. Here it is given that

$$\pi = 2.5 \text{ atm}, T = 24 + 273 = 297\text{K}, S = 0.0821 \text{ lit. atm. deg}^{-1} \text{ mol}^{-1}, C = ?$$

We know that $\pi = CST$

$$\text{or } C = \frac{\pi}{ST} = \frac{2.5}{0.0821 \times 297}$$

$$= 0.1025 \text{ moles/litre}$$

Ex.21 Twenty grams of a substance were dissolved in 500 ml. of water and the osmotic pressure of the solution was found to be 600 mm of mercury at 15°C. Determine the molecular weight of the substance-

(A) 1120

(B) 1198

(C) 1200

(D) None of these

(Ans. B)

Sol. Here it is given that

$$w = 20 \text{ gm} ; V = 500 \text{ ml.}$$

$$= \frac{500}{1000} = 0.5 \text{ litre}$$

$$\pi = 600 \text{ mm} = \frac{600}{760} \text{ atm} ;$$

$$T = 15 + 273 = 288^\circ\text{A}$$

$$m = ?$$

According to Van't Hoff equation ,

$$\pi V = nST \quad \pi V = \frac{w}{m} ST$$

$$\therefore m = \frac{wST}{\pi V} = \frac{20 \times 0.0821 \times 288 \times 760}{600 \times 0.5}$$

$$= 1198$$

Ex.22 Blood plasma has the following composition (milli-equivalents per litre). Calculate its osmotic pressure

at 37°C.

$\text{Na}^+ = 138$, $\text{Ca}^{2+} = 5.2$, $\text{K}^+ = 4.5$, $\text{Mg}^{2+} = 2.0$, $\text{Cl}^- = 105$, $\text{HCO}_3^- = 25$, $\text{PO}_4^{3-} = 2.2$, $\text{SO}_4^{2-} = 0.5$,
Proteins = 16, Others = 1.0

(A) 7.47 atm

(B) 7.30 atm

(C) 7.29 atm

(D) 7.40 atm

(Ans. A)

Sol. Since for calculating osmotic pressure we require millimoles/litre therefore

$$\text{Na}^+ = 138 \quad \text{Ca}^{2+} = \frac{5.2}{2} = 2.6, \quad \text{K}^+ = 4.5,$$

$$\text{Mg}^{2+} = \frac{2.0}{2} = 1.0, \quad \text{Cl}^- = 105,$$

$$\text{HCO}_3^- = 24, \text{PO}_4^{3-} = \frac{2.2}{3} = 0.73,$$

$$\text{SO}_4^{2-} = \frac{0.5}{2} = 0.25, \quad \text{Proteins} = 16,$$

others = 1.0

$$\text{Total} = 294.18 \text{ millimoles/litre} = \frac{294.18}{1000} = 0.294 \text{ moles/litre}$$

Now since $\pi = CST$

$$= 0.294 \times 0.0821 \times 310 = 7.47 \text{ atm}$$

Ex.23 0.15g of a substance dissolved in 15g of solvent boiled at a temperature higher by 0.216°C than that of the pure solvent. Calculate the molecular weight of the substance. Molal elevation constant for the solvent is 2.16°C.

(A) 216

(B) 100

(C) 178

(D) None of these

(Ans. B)

Sol. Here it is given that

$$w = 0.15 \text{ g},$$

$$\Delta T_b = 0.216^\circ\text{C}$$

$$W = 15\text{g}$$

$$K_b = 2.16^\circ\text{C}$$

$$m = ?$$

Substituting values in the expression ,

$$m = \frac{1000 \times K_b \times w}{\Delta T_b \times W}$$

$$m = \frac{1000 \times 2.16 \times 0.15}{0.216 \times 15} = 100$$

Ex.24 A solution of 0.450 gm of urea (mol. wt 60) in 22.5 g of water showed 0.170°C of elevation in boiling point. Calculate the molal elevation constant of water-

(A) 0.17°C

(B) 0.45°C

(C) 0.51°C

(D) 0.30°C **(Ans. C)**

Sol. Wt. of solute,

$$w = 0.450 \text{ g}$$

Wt. of solvent ,

$$W = 22.5 \text{ g}$$

Mol. wt of solute,

$$m = 60$$

Molal elevation constant $K_b = ?$

Boiling point elevation, $\Delta T_b = 0.170^\circ\text{C}$

Substituting these values in the equation-

$$K_b = \frac{m \times W \times \Delta T_b}{1000 \times w}$$

$$= \frac{60 \times 22.5 \times 0.170}{1000 \times 0.450} = 0.51^\circ\text{C}$$

Ex.25 Calculate the boiling point of a solution containing 0.45g of camphor (mol. wt. 152) dissolved in 35.4g of acetone (b.p. 56.3°C); K_b per 100 gm of acetone is 17.2°C .

(A) 56.446°C

(B) 52.401°C

(C) 56.146°C

(D) 50.464°C

Sol. Here it is given that

$w = 0.45 \text{ g}$, $W = 35.4$, $m = 152$,

$K_b = 17.2$ per 100gm

Now we know that $\Delta T_b = \frac{100 \times K_b \times w}{m \times W}$

(Note that this is expression when K_b is given per 100g of the solvent)

Substituting the values in the above expression.

$$\Delta T_b = \frac{100 \times 17.2 \times 0.45}{152 \times 35.4} = 0.146^\circ\text{C}$$

Now we know that

B.P. of solution (T) - B.P. of solvent (T_0) = ΔT

\therefore B.P. of solution (T) = B.P. of solvent (T_0) + ΔT

Hence B.P. of solution = $56.3 + 0.146$

= 56.446°C

Ex.26 The freezing point of 0.2 molal K_2SO_4 is -1.1°C . Calculate Van't Haff factor and percentage degree of dissociation of K_2SO_4 . K_f for water is 1.86°

(A) 97.5

(B) 90.75

(C) 105.5

(D) 85.75 **(Ans. A)**

Sol. $\Delta T_f = \text{freezing point of water} - \text{freezing point of solution} = 0^\circ\text{C} - (-1.1^\circ\text{C}) = 1.1^\circ$

We know that,

$$\Delta T_f = i \times K_f \times m$$

$$1.1 = i \times 1.86 \times 0.2$$

$$\therefore i = \frac{1.1}{1.86 \times 0.2} = 2.95$$

But we know

$$i = 1 + (n - 1)\alpha$$

$$2.95 = 1 + (3 - 1)\alpha = 1 + 2\alpha$$

$$\alpha = 0.975$$

Van't Haff factor (i) = 2.95

Degree of dissociation = 0.975

Percentage degree of dissociation = **97.5**

Ex.27 The density of a 3M sodium thiosulphate solution ($\text{Na}_2\text{S}_2\text{O}_3$) is 1.25 g/mL. Calculate (i) the percentage by mass of sodium thiosulphate, (ii) the mole fraction of sodium thiosulphate and (iii) molalities of Na^+ and $\text{S}_2\text{O}_3^{2-}$ ions -

Sol. (i) Mass of 1000 mL of $\text{Na}_2\text{S}_2\text{O}_3$ solution

$$= 1.25 \times 1000 = 1250 \text{ g}$$

Mass of $\text{Na}_2\text{S}_2\text{O}_3$ in 1000 mL of 3M solution

$$= 3 \times \text{Mol. mass of } \text{Na}_2\text{S}_2\text{O}_3$$

$$= 3 \times 158 = 474 \text{ g}$$

Mass percentage of $\text{Na}_2\text{S}_2\text{O}_3$ in solution

$$= \frac{474}{1250} \times 100 = 37.92$$

Alternatively, $M = \frac{x \times d \times 10}{m_A}$

$$3 = \frac{x \times 1.25 \times 10}{158}$$

$$x = 37.92$$

(ii) No. of moles of $\text{Na}_2\text{S}_2\text{O}_3 = \frac{474}{158} = 3$

Mass of water = $(1250 - 474) = 776 \text{ g}$

No. of moles of water = $\frac{776}{18} = 43.1$

Mole fraction of $\text{Na}_2\text{S}_2\text{O}_3$

$$= \frac{3}{43.1 + 3} = \frac{3}{46.1} = 0.065$$

(iii) No. of moles of Na^+ ions

$$= 2 \times \text{No. of moles of } \text{Na}_2\text{S}_2\text{O}_3$$

$$= 2 \times 3 = 6$$

Molality of Na^+ ions

$$= \frac{\text{No. of moles of } \text{Na}^+ \text{ ions}}{\text{Mass of water in kg}}$$

$$= \frac{6}{776} \times 1000$$

$$= 7.73 \text{ m}$$

No. of moles of $\text{S}_2\text{O}_3^{2-}$ ions = No. of moles of $\text{Na}_2\text{S}_2\text{O}_3 = 3$

Molality of $\text{S}_2\text{O}_3^{2-}$ ions = $\frac{3}{776} \times 1000 = 3.86 \text{ m}$

Ex.28 A solution is prepared by dissolving 5.64 gm of glucose in 60g of water. Calculate the following.

- (i) mass per cent of each of glucose and water,
- (ii) molality of the solution,
- (iii) mole fraction of each of glucose and water.

Sol. (i) Total mass of solution

$$= 5.64 + 60 = 65.64 \text{ g}$$

$$\text{Mass per cent of glucose} = \frac{5.64}{65.64} \times 100$$

$$= 8.59\%$$

Mass per cent of water

$$= (100 - \text{Mass per cent of glucose})$$

$$= (100 - 8.59) = 91.41\%$$

$$(ii) \text{ No. of moles of glucose} = \frac{5.64}{180}$$

$$\text{Mass of water in kg} = \frac{60}{1000}$$

$$\text{Molality} = \frac{5.64}{180} \times \frac{1000}{60} = 0.522 \text{ m}$$

$$(iii) \text{ No. of moles of glucose} = \frac{5.64}{180} = 0.0313$$

$$\text{No. of moles of water} = \frac{60}{18} = 3.333$$

Mole fraction of glucose

$$= \frac{0.0313}{3.333 + 0.0313} = 0.0093$$

$$\text{Mole fraction of water} = \frac{3.333}{3.333 + 0.0313}$$

$$= 0.9907$$

Ex.29 The volume of water which must be added to a mixture of 350 cm³ of 6 M HCl and 650 ml of 3 M HCl to get a resulting solution of 3 M concentration is

[Ans. D]

(A) 75 mL

(B) 150 mL

(C) 100 mL

(D) 350 mL

Sol. Molarity of mixture of 6 M and 3 M HCl

$$= \frac{350 \times 6 + 650 \times 3}{1000} = 4.05 \text{ M}$$

Now, apply dilution formula

$$M_1V_1 = M_2V_2 \text{ or } V_2 = \frac{4.05 \times 1000}{3}$$

$$= 1350 \text{ ml}$$

Volume of water to be added

$$= 1350 - 1000 = 350 \text{ ml}$$

Ex.30 The mole fraction of CH_3OH in an aqueous solution is 0.02 and its density is 0.994 g cm^{-3} . Determine its molarity and molality.

Sol. Let x mole of CH_3OH and y mole of water be present in solution.

$$\text{Mole fraction of } \text{CH}_3\text{OH} = \frac{x}{x+y} = 0.02$$

$$\text{So, } \frac{y}{x} = 49 \text{ or } \frac{x}{y} = \frac{1}{49}$$

$$\text{Molality} = \frac{x}{18 \times y} \times 1000 = \frac{1000}{18 \times 49} = 1.13 \text{ m}$$

$$\text{Volume of solution} = \frac{\text{Total mass}}{\text{density}}$$

$$= \frac{32x + 18y}{0.994} \text{ mL}$$

$$= \frac{32x + 18y}{0.994 \times 1000} \text{ litre} = \frac{32x + 18y}{994} \text{ litre}$$

$$\text{Molarity} = \frac{x}{32x + 18y} \times 994$$

$$= \frac{994}{32 + 18 \times y/x} = \frac{994}{32 + 18 \times 49} = 1.0875 \text{ M}$$

Ex.31 Calculate the concentration of NaOH solution in g/mL which has the same normality as that of a solution of HCl of concentration 0.04 g/mL . -

$$\text{Sol. } N_{\text{HCl}} = \frac{w_B \times 1000}{E_B \times V} = \frac{0.04 \times 1000}{36.5 \times 1} = 1.095$$

$$N_{\text{NaOH}} = N_{\text{HCl}}$$

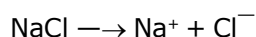
$$\therefore 1.095 = \frac{w_B \times 1000}{40 \times 1}$$

$$w_B = 0.0438 \text{ g/mL}$$

Ex.32 How many Na^+ ions are present in 50 mL of a 0.5 M solution of NaCl ?

$$\text{Sol. } \text{Number of moles of NaCl} = \frac{MV}{1000}$$

$$= \frac{0.5 \times 50}{1000} = 0.025$$



Number of moles Na^+ = Number of moles of NaCl

$$= 0.025$$

$$\text{Number of ions of } \text{Na}^+ = 0.025 \times 6.023 \times 10^{23}$$

$$= 1.505 \times 10^{22}$$

Ex.33 250 mL of a Na_2CO_3 solution contains 2.65 g of Na_2CO_3 . 10 mL of this solution is added to x mL of water to obtain 0.001 M Na_2CO_3 solution. The value of x is :

(Molecular mass of $\text{Na}_2\text{CO}_3 = 106 \text{ amu}$)-

(A) 1000

(B) 990

(C) 9990

(D) 90

Sol.[B] Molarity of solution

$$M = \frac{w_B \times 1000}{m_B \times V} = \frac{2.65 \times 1000}{106 \times 250} = 0.1$$

$$M_1 V_1 = M_2 V_2$$

$$0.1 \times 10 = 0.001 (10 + x)$$

$$x = 990 \text{ mL}$$

Ex.34 The volumes of two HCl solutions A (0.5 N) and B (0.1 N) to be mixed for preparing 2 L of 0.2 N HCl are -

(A) 0.5 L of A + 1.5 L of B

(B) 1.5 L of A + 0.5 L of B

(C) 1 L of A + 1 L of B

(D) 0.75 L of A + 1.25 L of B

Sol.(A) Let x L of A and (2 - x) L of B are mixed.

$$M_1 V_1 + M_2 V_2 = M_R (V_1 + V_2)$$

$$0.5 \times x + 0.1 (2 - x) = 0.2 \times 2$$

$$(0.5 - 0.1) x = 0.4 - 0.2$$

$$0.4 x = 0.2$$

$$x = 0.5 \text{ L}$$

\therefore 0.5 L of A and 1.5 L of B should be mixed.

Ex.35 Lowering of vapour pressure due to a solute in 1 molal aqueous solution at 100°C is -

(A) 13.44 mm Hg

(B) 14.12 mm Hg

(C) 31.2 mm Hg

(D) 35.2 mm Hg

Sol.(A) $m = \frac{x_B \times 1000}{(1 - x_B)m_A}$ x_B = mole fraction of solute

$$1 = \frac{x_B \times 1000}{(1 - x_B) \times 18} \quad m_A = \text{molar mass of solvent}$$

$$x_B = 0.0176$$

$$x_A = 1 - 0.0176 = 0.9824$$

$$p = p_0 x_A$$

$$= 760 \times 0.9824 = 746.62$$

$$\Delta p = p_0 - p = 760 - 746.62$$

$$= 13.4$$

Ex.36 The mass of a non-volatile solute (molecular mass = 40) which should be dissolved in 114 g octane to reduce its vapour pressure to 80% will be -

(A) 20 g

(B) 30 g

(C) 10 g

(D) 40 g

Sol.(C) If $p_0 = 100$, then $p = 80$

$$p = p_0 x_A$$

$$80 = 100 \times x_A$$

$$x_A = 0.80$$

$$x_A = \frac{n_A}{n_A + n_B} = \frac{114/114}{114/114 + w_B/40}$$

$$0.8 = \frac{1}{1 + w_B/40}$$

$$1 + \frac{w_B}{40} = \frac{1}{0.8}$$

$$w_B = 10 \text{ g}$$

Ex.37 A solution of urea in water has boiling point of 100.15°C . Calculate the freezing point of the same solution if K_f and K_b for water are $1.87 \text{ K kg mol}^{-1}$ and $0.52 \text{ K kg mol}^{-1}$ respectively -

Sol. $\Delta T_b = (100.15 - 100) = 0.15^\circ\text{C}$

We know that, $\Delta T_b = \text{molality} \times K_b$

$$\text{Molality} = \frac{\Delta T_b}{K_b} = \frac{0.15}{0.52} = 0.2884$$

$$\Delta T_f = \text{molality} \times K_f$$

$$= 0.2884 \times 1.87 = 0.54^\circ\text{C}$$

Thus, the freezing point of the solution

$$= -0.54^\circ\text{C}.$$

Ex.38 Calculate the molal depression constant of a solvent which has freezing point 16.6°C and latent heat of fusion 180.75 J g^{-1} -

Sol.
$$K_f = \frac{RT_f^2}{1000 \times L_f}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1},$$

$$T_f = 16.6^\circ\text{C} = 273 + 16.6 = 289.6 \text{ K},$$

$$L_f = 180.75 \text{ J g}^{-1}$$

Substituting the values in the above equation,

$$K_f = \frac{8.314 \times (289.6)^2}{1000 \times 180.75} = 3.86$$

Ex.39 The freezing point depression of $0.001 \text{ m } K_x[Fe(CN)_6]$ is $7.10 \times 10^{-3} \text{ K}$. Determine the value of x . Given, $K_f = 1.86 \text{ K kg mol}^{-1}$ for water -

Sol. $\Delta x = i \times K_f \times m$

$$7.10 \times 10^{-3} = i \times 1.86 \times 0.001$$

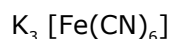
$$i = 3.817$$

$$\alpha = \frac{i-1}{n-1}$$

$$1 = \frac{3.817-1}{(x+1)-1}$$

$$x = 2.817 = 3$$

\therefore Molecular formula of the compound is



Ex.40 A certain substance 'A' tetramerises in water to the extent of 80%. A solution of 2.5 g of A in 100 g of water lowers the freezing point by 0.3°C . The molar mass of A is -

(A) 122

(B) 31

(C) 244

(D) 62

Sol.(D) $\alpha = \frac{1-i}{1-\frac{1}{n}}$

$$0.8 = \frac{1-i}{1-\frac{1}{4}}; i = 0.4$$

$$\Delta T = iK_f \times m$$

$$0.3 = 0.4 \times 1.86 \times \frac{w_B \times 1000}{m_B \times w_A}$$

$$0.3 = 0.4 \times 1.86 \times \frac{2.5 \times 1000}{m_B \times 100}$$

$$m_B = 62$$

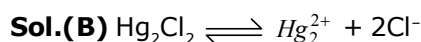
Ex.41 van't Hoff factor of Hg_2Cl_2 in its aqueous solution will be (Hg_2Cl_2 is 80% ionized in the solution) -

(A) 1.6

(B) 2.6

(C) 3.6

(D) 4.6



$$n = 3$$

$$\alpha = \frac{i-1}{n-1}$$

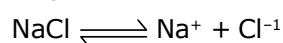
$$0.8 = \frac{i-1}{3-1}$$

$$i = 2.6$$

Ex.42 Calculate the amount of NaCl which must be added to 100 g water so that freezing point is depressed by 2K. For water, $K_f = 1.86 \text{ K kg mol}^{-1}$ -

Sol. NaCl is a strong electrolyte. It is completely dissociated in solution.

Degree of dissociation, $\alpha = 1$



$$(n = 2)$$

$$\text{No. of particles after dissociation} = 1 + (n - 1) \alpha$$

$$= 1 + (2 - 1) \times 1 = 2$$

$$\frac{\Delta T_{obs.}}{\Delta T_{theo.}} = \frac{\text{No. of particles after dissociation}}{\text{No. of particles when there is no dissociation}}$$

$$\frac{2}{\Delta T_{theo.}} = 2$$

$$\text{or } \Delta T_{theo.} = 1$$

Let w g of NaCl be dissolved in 100 g of water.

$$\text{So, } \Delta T_{theo.} = \frac{1000 \times K_f \times w}{W \times m}$$

$$\text{or } w = \frac{\Delta T_{theo.} \times W \times m}{1000 \times K_f} = \frac{1 \times 100 \times 58.5}{1000 \times 1.86}$$

$$= 3.145 \text{ g}$$

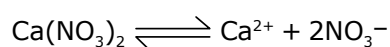
Ex.43 The degree of dissociation of $\text{Ca}(\text{NO}_3)_2$ in a dilute solution containing 14 g of the salt per 200 g of water at 100°C is 70%. If the vapour pressure of water is 760 mm, calculate the vapour pressure of solution -

Sol. $\Delta p_{theo.}$ = Lowering in vapour pressure when there is no dissociation

$$= p_o \times \frac{wM}{Wm} \quad (\text{given, } p_o = 760 \text{ mm, } w = 14 \text{ g, } W = 200 \text{ g, } M = 18, m = 164)$$

$$= \frac{760 \times 14 \times 18}{200 \times 164} = 5.84 \text{ mm}$$

$$\text{Degree of dissociation} = \frac{70}{100} = 0.7$$



$$(n = 3)$$

$$\frac{\Delta p_{obs.}}{\Delta p_{theo.}} = \frac{\text{No. of particles after dissociation}}{\text{No. of particles when there is no dissociation}}$$

$$= \frac{1 + (n-1)\alpha}{1} = \frac{1 + (3-1) \times 0.7}{1} = 2.4$$

$$\text{So, } \Delta p_{obs.} = 2.4 \times \Delta p_{theo.} = 2.4 \times 5.84 = 14.02 \text{ mm}$$

$$p_0 - p_s = \Delta p_{obs.} = 14.02$$

$$p_s = p_0 - 14.02 = 760 - 14.02 = 745.98 \text{ mm}$$

Ex.44 Calculate the normal boiling point of a sample of sea water found to contain 3.5% of NaCl and 0.13% of MgCl_2 by mass. The normal boiling point of water is 100°C and K_b (water) = $0.51 \text{ K kg mol}^{-1}$. Assume that both the salts are completely ionised -

Sol. Mass of NaCl = 3.5 g

$$\text{No. of moles of NaCl} = \frac{3.5}{58.5}$$

Number of ions furnished by one molecule of NaCl is 2.

$$\text{So, actual number of moles of particles furnished by sodium chloride} = 2 \times \frac{3.5}{58.5}$$

$$\text{Similarly, actual number of moles of particles furnished by magnesium chloride} = 3 \times \frac{0.13}{95}$$

$$\text{Total number of moles of particles} = \left(2 \times \frac{3.5}{58.5} + 3 \times \frac{0.13}{95} \right)$$

$$= 0.1238$$

$$\text{Mass of water} = (100 - 3.5 - 0.13) = 96.37 \text{ g} = \frac{96.37}{1000} \text{ kg}$$

$$\text{Molality} = \frac{0.1238}{96.37} \times 1000 = 1.2846$$

$$\Delta T_b = \text{Molality} \times K_b$$

$$= 1.2846 \times 0.51 = 0.655 \text{ K}$$

Hence, boiling point of sea water = 373.655 K or 100.655°C .

Ex.45 Sea water is 3.5% by mass of a salt and has a density 1.04 g cm^{-3} at 293 K . Assuming the salt to be sodium chloride, calculate the osmotic pressure of sea water. Assume complete ionisation of the salt -

Sol. Mass of NaCl = 3.5 g

$$\text{No. of moles} = \frac{3.5}{58.5}$$

Actual number of moles of particles of solute in solution.

$$= \frac{2 \times 3.5}{58.5}$$

$$\text{Volume of solution} = \frac{100}{1.04 \times 1000} \text{ litre}$$

$$\pi = \frac{2 \times 3.5}{58.5} \times \frac{1.04 \times 1000}{100} \times 0.0821 \times 293 = 29.93 \text{ atm.}$$

Ex.46 Molality of a solution in aqueous medium is 0.8. Calculate its mole fraction and the percentage by mass of solute if molar mass of solute is 60 -

Sol. We know that,

$$m = \frac{x_B \times 1000}{(1 - x_B) \times m_A} \quad \dots(i)$$

where, x_B = mole fraction of solute

m_A = molar mass of solvent

$$0.8 = \frac{x_B \times 1000}{(1 - x_B) \times 18}$$

$$x_B = 0.014$$

Let $w_B = x$ g, $w_A = 100$ g

$$m = \frac{w_B \times 1000}{m_B \times w_A}$$

$$0.8 = \frac{x \times 1000}{60 \times 100}$$

$$x = 4.8\%$$

Ex.47 A very small amount of a non-volatile solute (that does not dissociate) is dissolved in 56.8 cm³ of benzene (density 0.889 g cm⁻³). At room temperature, vapour pressure of this solution is 98.8 mm Hg while that of benzene is 100 mm Hg. Find the molality of the solution. If the freezing temperature of this solution is 0.73 degree lower than that of benzene, what is the value of molal freezing point depression constant of benzene ?

Sol. $\frac{\Delta p}{p_0} = X_A$

$$\frac{100 - 98.8}{100} = X_A$$

$$X_A = 0.012$$

$$\text{Molality} = \frac{X_A \times 1000}{(1 - X_A)m_B} = \frac{0.012 \times 1000}{0.988 \times 78} = 0.1557$$

$$\Delta T = K_f \times \text{Molality}$$

$$0.73 = K_f \times 0.1557$$

$$K_f = 4.688$$

Ex.48 x g of a non-electrolytic compound (molar mass = 200) is dissolved in 1.0 litre of 0.05 M NaCl solution. The osmotic pressure of this solution is found to be 4.92 atm at 27°C. Calculate the value of 'x'. Assume complete dissociation of NaCl and ideal behaviour of this solution.

- (A) 16.52 gm (B) 24.032 gm
(C) 19.959 gm (D) 12.35 gm

Sol.(C)(i) For NaCl : $\pi = iCRT = 2 \times 0.05 \times 0.0821 \times 300 = 2.463 \text{ atm}$

(ii) For unknown compound,

$$\pi = CRT = \frac{x}{200} \times 0.0821 \times 300 = 0.1231 \times \text{atm}$$

Total osmotic pressure $\pi = \pi_1 + \pi_2$

$$4.92 = 2.463 + 0.1231 \times$$

$$x = 19.959 \text{ g}$$

Ex.49 The freezing point of a solution containing 50 cm³ of ethylene glycol in 50 g of water is found to be – 34°C. Assuming ideal behaviour, calculate the density of ethylene glycol (K_f for water = 1.86 K kg mol⁻¹) -

- (A) 1.13 g/cm³ (B) 2.00 g/cm³ (C) 1.8 g/cm³ (D) 2.25 g/cm³

Sol. $\Delta T = K_f \times \frac{w \times 1000}{m \times W}$

$$34 = 1.86 \times \frac{w \times 1000}{62 \times 50}$$

$$w = 56.66 \text{ g}$$

$$V = \frac{w}{d}, 50 = \frac{56.66}{d}$$

$$d = 1.13 \text{ g/cm}^3$$

Ex.50 Match the boiling point with K_b for x, y and z if molecular weight of x, y and z are same.

	b. pt	K_b
x	100	0.68
y	27	0.53
z	253	0.98

- (A) (B) (C) (D)

Sol. Molal elevation constant may be calculated as,

$$K_{b_{1000}} = \frac{RT_0^2}{1000L_v} \text{ (where, } T_0 = \text{boiling point of pure solvent } L_v = \text{latent heat of vaporization.)}$$

$$= \frac{RT_0^2}{1000 \frac{\Delta H_v}{m_B}} L_v = \frac{\Delta H_v}{m_B}$$

(here, ΔH_v = molar latent heat of vaporization).

$$= \frac{RT_0^2 m_B}{1000 \Delta H_v} m_B = \text{molar mass of solute.}$$

$$K_{b_{1000}} = \frac{RT_0 m_B}{1000 \Delta S_v} \text{ here, } \Delta S_v = \text{entropy of vaporization.}$$

By considering ΔS_v as almost constant, $K_b \propto T_0$.

$$\therefore K_b(x) = 0.68 ; K_b(y) = 0.53 \text{ and } K_b(z) = 0.98.$$

Ex.51 1.22 g C_6H_5COOH is added into two solvents and data of ΔT_b and K_b are given as -

(A) In 100 g CH_3COCH_3 ; $\Delta T_b = 0.17$; $K_b = 1.7$ kg kelvin/mol

(B) In 100 g benzene; $\Delta T_b = 0.13$; $K_b = 2.6$ kg kelvin/mol

Find out the molecular weight of C_6H_5COOH in both cases and interpret the result.

Sol. (a) $\Delta T = K_b \times \frac{w_B \times 1000}{m_B \times w_A}$

$$0.17 = 1.7 \times \frac{1.22 \times 1000}{m_B \times 100}$$

$$m_B = 122$$

(b) $\Delta T = \frac{K_b \times w_B \times 1000}{m_B \times w_A}$

$$0.13 = \frac{2.6 \times 1.22 \times 1000}{m_B \times 100}$$

$$m_B = 244$$

(Abnormally double molecular mass of benzoic acid, it shows association of benzoic acid in benzene).

Ex.52 How much C_2H_5OH should be added to 1 litre H_2O so that it will not freeze at $-20^\circ C$?

$$K_f = 1.86^\circ C/m$$

Sol. Mass of 1 litre water = 1000 g

$$\therefore \Delta T = K_f \times \frac{w_B \times 1000}{m_B \times w_A}$$

$$20 = 1.86 \times \frac{w_B \times 1000}{46 \times 1000}$$

$$w_B = 494.6 \text{ g}$$

Ex.53 Calculate the molarity of each of the ions in solution when 3.0 litre of 4.0 M NaCl and 4.0 litre of 2.0 M $CoCl_2$ are mixed and diluted to 10 litre -

Sol. Molarity $Na^+ = 1.2$ M

Molarity $Co^{2+} = 0.8$ M

Molarity $Cl^- = 2.8$ M

NaCl	= Na ⁺	Cl ⁻
1 mole	1 mole	1 mole
3 × 4 mole	12 mole	12 mole
CoCl ₂	= Co ²⁺	+ 2Cl ⁻
1 mole	1 mole	2 mole
2 × 4 mole	8 mole	16 mole

Total Cl⁻ ions = 28 mole.

Ex.54 Calculate the molarity of each ion in solution after 2.0 litre of 3.0 M AgNO₃ is mixed with 3.0 litre of 1.0 M BaCl₂.

Sol.

BaCl ₂	+	2AgNO ₃	→	2AgCl↓	+	Ba(NO ₃) ₂	
Initial		3		6		-	-
mole							
Final		-		-		6 (ppt)	3
mole							

$$M_{Ba^{2+}} = \frac{\text{mole}}{\text{Total vol.}} \times \frac{3}{5} M_{NO_3^-} = \frac{6}{5}$$

Ex.55 1.2 kg ethylene glycol $\begin{bmatrix} CH_2OH \\ | \\ CH_2OH \end{bmatrix}$ was added in a car radiator containing 9 litre water. The freezing of water was just prevented when car was running in the Himalayan valley at temperature - 4°C. Sudden thunderstorm in the valley lowered the temperature to -6°C. Calculate the amount of ice separated.

Sol. $\Delta T = K_f \times \frac{w_A \times 1000}{m_A \times w_B}$ A → Solute; B → Solvent

$$6 = 1.86 \times \frac{1200 \times 1000}{62 \times w_B}$$

$$w_B = 6000 \text{ g}$$

$$I_{\text{weight of ice}} = \text{Total weight of H}_2\text{O} - \text{wt. of H}_2\text{O at } -6^\circ\text{C} = 9000 - 6000 = 3000 \text{ g} = 3 \text{ kg}$$

Ex.56 The vapour pressure of a solvent decreased by 10 mm of mercury when a non-volatile solute was added to the solvent. The mole fraction of the solute in the solution is 0.2. What should be the mole fraction of the solvent, if the decrease in the vapour pressure is to be 20 mm of mercury -

- (A) 0.8 (B) 0.6 (C) 0.4 (D) 0.2

Sol. [B] Mole fraction of solute = $\frac{\text{lowering in vapour pressure}}{\text{vapour pressure of solvent}}$

Comparing under the two conditions,

$$\frac{0.2}{\text{mole fraction of solute}} = \frac{10}{20}$$

or mole fraction of solute = 0.4

mole fraction of solvent = $(1 - 0.4) = 0.6$

Ex.57 Three solutions of HCl having normality 12 N, 6 N and 2 N are mixed to obtain a solution of 4 N normality. Which among the following volume ratio is correct for the above three components ?

- (A) 1 : 1 : 5 (B) 1 : 2 : 6 (C) 2 : 1 : 9 (D) 1 : 2 : 4

Sol. [B] Use Hit & Trial Method.

$$N_1V_1 + N_2V_2 + N_3V_3 = N_R(V_1 + V_2 + V_3)$$

$$12 \times 1 + 6 \times 2 + 2 \times 6 = N_R(9)$$

$$N_R = 4$$

Ex.58 Two solutions of H_2SO_4 of molarities x and y are mixed in the ratio of V_1 mL : V_2 mL to form a solution of molarity M_1 . If they are mixed in the ratio of V_2 mL : V_1 mL, they form a solution of molarity M_2 . Given

V_1 . Given $V_1/V_2 = \frac{x}{y} > 1$ and $\frac{M_1}{M_2} = \frac{5}{4}$, then $x : y$ is -

- (A) 2 : 1 (B) 4 : 1 (C) 1 : 2 (D) 3 : 1

Sol. Molarity of the mixture can be calculated as.

$$M_1V_1 + M_2V_2 = M_R(V_1 + V_2)$$

where, M_R = resultant solution

$$V_1 \times x + V_2 \times y = M_1(V_1 + V_2)$$

$$V_2 \times x + V_1 \times y = M_2(V_1 + V_2)$$

Dividing equation (i) by equation (ii), we get

$$\frac{V_1x + V_2y}{V_2x + V_1y} = \frac{M_1}{M_2}$$

Substituting $\frac{M_1}{M_2} = \frac{5}{4}$ and $\frac{V_1}{V_2} = \frac{x}{y}$ we can calculate $x : y$.

Ex.59 Insulin ($C_{21}H_{39}O_6$) is dissolved in a suitable solvent and the osmotic pressure (π) of solutions of various concentrations (g/cc) C is measured at 20°C . The slope of the plot of π against ' C ' is found to be 4.65×10^{-3} . The molecular weight of insulin is -

- (A) 4.8×10^5 (B) 9×10^5 (C) 3×10^5 (D) 5.17×10^6

Sol. [D] $\pi V = \frac{w_B}{m_B} \times RT$

$$\pi = \left(\frac{w_B}{V} \right) \frac{RT}{m_B}$$

$$\pi = C \times \frac{RT}{m_B} \times 1000 \quad \dots(i)$$

where C = concentration in g/cc,

Comparing eqs. (i) and (ii), $\dots(ii)$

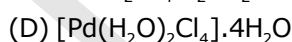
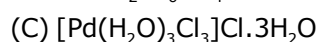
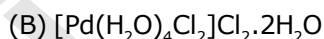
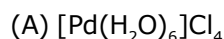
$$\text{Slope} = \frac{RT}{m_R} \times 1000$$

$$m_B = \frac{RT}{\text{Slope}} \times 1000$$

$$= \frac{0.0821 \times 293 \times 1000}{4.65 \times 10^{-3}}$$

$$= 5.17 \times 10^6 \text{ J}$$

Ex.60 Compound $\text{PdCl}_4 \cdot 6\text{H}_2\text{O}$ is a hydrated complex; 1 molal aqueous solution of it has freezing point 269.28 K. Assuming 100% ionization of complex, calculate the molecular formula of the complex (K_f for water = $1.86 \text{ K kg mol}^{-1}$) -



Sol. [C] $\Delta T = i \times K_f \times m$

$$(273 - 269.28) = i \times 1.86 \times 1$$

$$3.72 = i \times 1.86$$

$$i = 2$$

$$\alpha = \frac{i-1}{n-1}$$

$$1 = \frac{2-1}{n-1} \text{ or } n = 2.$$

Thus, the complex should give two ions in the solution, i.e., the complex will be $[\text{Pd}(\text{H}_2\text{O})_3\text{Cl}_3]\text{Cl} \cdot 3\text{H}_2\text{O}$

Ex.61 pH of 0.1 M monobasic acid is measured to be 2. Its osmotic pressure at a given temperature T K is -

(A) 0.1 RT

(B) 0.11 RT

(C) 1.1 RT

(D) 0.01 RT

Sol. [B] $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$

$$t = 0 \quad C \quad 0 \quad 0$$

$$t_{\text{eq}} \quad C - C\alpha \quad C\alpha \quad C\alpha$$

$$[\text{H}^+] = C\alpha, [\text{H}^+] = 10^{-\text{pH}}$$

$$\therefore C\alpha = 10^{-2}$$

$$0.1 \alpha = 10^{-2}$$

$$\alpha = 0.1$$

$$\alpha = \frac{i-1}{n-1}; 0.1 = \frac{i-1}{2-1}$$

$$i = 1.1$$

$$\therefore \pi = iCRT$$

$$= 1.1 \times 0.1 \times RT = 0.11 RT$$

Ex.62 Lowering of vapour pressure in 1 molal aqueous solution at 100°C is -

- (A) 13.44 mm Hg (B) 14.12 mm Hg (C) 31.2 mm Hg (D) 35.2 mm Hg

Sol. [A] Molality and mole fraction are related as follows :

$$m = \frac{x_B \times 1000}{(1 - x_B)m_A} \quad m = 1$$

$$1 = \frac{x_B \times 1000}{(1 - x_B) \times 18} \quad x_B = \text{mole fraction of solute}$$

$$m_A = \text{molar mass of solvent}$$

$$x_B = 0.0176, x_A = 0.9824$$

$$p = p_0 x_A$$

$$p = 760 \times 0.9824 = 746.624$$

$$\Delta p = p_0 - p = 760 - 746.624 = 13.4 \text{ mm Hg.}$$

Ex.63 Molarity and molality of a solution of caustic soda are respectively 11.12 M and 94.12 m. The density of the solution is -

- (A) 0.556 g mL⁻¹ (B) 5.56 g mL⁻¹
(C) 55.6 g mL⁻¹ (D) none of these

Sol. [A] $d = M \left(\frac{1}{m} + \frac{\text{molar mass of solute}}{1000} \right)$

$$d = 11.12 \left(\frac{1}{94.12} + \frac{40}{1000} \right)$$

$$= 0.556 \text{ g mL}^{-1}$$

Thought – 7

The properties such as boiling point, freezing point and vapour pressure of pure solvent change when solute molecules are added to get homogeneous solution. These are called colligative properties. Application of colligative properties are very useful in day-to-day life. One of its examples is the use of ethylene glycol and water mixture as anti-freezing liquid in the radiator of automobiles.

A solution M is prepared by mixing ethanol and water.

The mole fraction of ethanol in the mixture is 0.9.

Given : Freezing point depression constant of water (K_f for water) = 1.86 K kg mol⁻¹.

Freezing point depression constant of ethanol (K_f for ethanol) = 2.0 K kg mol⁻¹

Boiling point elevation constant of water (K_b for water) = $0.52 \text{ K kg mol}^{-1}$.

Boiling point elevation constant of ethanol (K_b for ethanol = $1.2 \text{ K kg mol}^{-1}$)

Standard freezing point of water = 273 K

Standard freezing point of ethanol = 155.7 K

Standard boiling point of water = 373 K

Standard boiling point of ethanol = 351.5 K

Vapour pressure of pure water = 32.8 mm Hg

Vapour pressure of pure ethanol = 40 mm Hg

Molecular weight of water = 18 g mol^{-1}

Molecular weight of ethanol = 46 g mol^{-1}

In answering the following questions, consider the solutions to be ideal dilute solutions and solutes to be non-volatile and non-dissociative.

Ex.64 The freezing point of the solution M is -

- (A) 268.7 K (B) 268.5 K (C) 234.2 K (D) 150.9 K

Sol. [D] Molality $m = \frac{x_B \times 1000}{(1 - x_B)m_A} = \frac{0.1 \times 1000}{0.9 \times 46}$

$$= 2.415$$

$$\Delta T = K_f \times m$$

$$= 2 \times 2.415 = 4.83$$

$$\text{Freezing point of solution} = 155.7 - 4.83 = 150.9 \text{ K.}$$

Ex.65 The vapour pressure of the solution M is -

- (A) 39.3 mm Hg (B) 36.0 mm Hg (C) 29.5 mm Hg (D) 28.8 mm Hg

Sol. [B] $p = p^0 x_A$

$$= 40 \times 0.9 = 36 \text{ mm Hg}$$

Ex.66 Water is added to the solution M such that the mole fraction of water in the solution becomes 0.9. The boiling point of this solution is -

- (A) 380.4 K (B) 376.2 K (C) 375.5 K (D) 354.7 K

Sol. [B] When water becomes solvent, then molality of solution will be.

$$m = \frac{x_B \times 100}{x_A \times m_A} = \frac{0.1 \times 1000}{0.9 \times 18} = 6.172$$

$$\Delta T = K_b \times m = 0.52 \times 6.172 = 3.209$$

$$\text{Boiling point of solution} = 373 + 3.209 = 376.2 \text{ K}$$

Exercise - I**(Only one option is correct)**

1. Select correct statement -
 (A) b.p. of 1 molal NaCl solution is twice that of 1 molal sucrose solution
 (B) b.p. elevation of 1 molal glucose solution is half of the 1 molal KCl solution
 (C) b.p. is a colligative property
 (D) All of the above

Sol.

2. Total vapour pressure of mixture of 1 mol volatile component A ($p_A^0 = 100$ mmHg) and 3 mol of volatile component B ($p_B^0 = 60$ mmHg) is 75 mm. For such case -
 (A) there is positive deviation from Raoult's law
 (B) boiling point has been lowered
 (C) force of attraction between A and B is smaller than that between A and A or between B and B
 (D) All the above statements are correct

Sol.

3. At a given temperature, total vapour pressure in Torr of a mixture of volatile components A and B is given by $P = 120 - 75 X_B$
 hence, vapour pressure of pure A and B respectively (in Torr) are -
 (A) 120, 75 (B) 120, 195
 (C) 120, 45 (D) 75, 45

Sol.

4. Van't Hoff factors of aqueous solutions of X, Y, Z are 1.8, 0.8 and 2.5. Hence their -
 (A) b.p. : $Y < X < Z$
 (B) osmotic pressure : $X = Y = Z$
 (C) v.p. : $Y < X < Z$
 (D) None of these

Sol.

5. Decimolar solution of potassium ferricyanide, $K_3[Fe(CN)_6]$ has osmotic pressure of 3.94 atm at 27°C. Hence percent ionisation of the solute is -
 (A) 10% (B) 20%
 (C) 30% (D) 40%

Sol.

6. An aqueous solution of urea containing 18 g urea in 1500 cm³ of solution has a density of 1.052 g/cm³. If the molecular weight of urea is 60, then the molality of solution is -
 (A) 0.2 (B) 0.192
 (C) 0.064 (D) 1.2

Sol.

7. 2.56 g of sulphur in 100 g of CS_2 has depression in f.p. of 0.010° , $K_f = 0.1^\circ (\text{molal})^{-1}$. Hence, atomicity of sulphur is -
(A) 2 (B) 4 (C) 6 (D) 8

Sol.

8. Consider following solutions -
I : 1 M a glucose
II. : 1 M a sodium chloride
III. : 1 M benzoic acid in benzene
IV. : 1 M ammonium phosphate
Select incorrect statement -
(A) all are isotonic solutions
(B) III is hypotonic of I, II, IV
(C) I, II, IV are hypertonic of III
(D) IV is hypertonic of I, II, III

Sol.

9. The relationship between osmotic pressure at 273 K when 10 g glucose (P_1) 10 g urea (P_2) and 10 g sucrose (P_3) are dissolved in 250 ml of water is -
(A) $P_1 > P_2 > P_3$ (B) $P_3 > P_1 > P_2$
(C) $P_2 > P_1 > P_3$ (D) $P_2 > P_3 > P_1$

Sol.

10. The osmotic pressure of a solution of benzoic acid dissolved in benzene is less than expected because -
(A) Benzoic acid is an organic solute
(B) Benzene is a non-polar solvent
(C) Benzoic acid dissociates in benzene
(D) Benzoic acid gets associated in benzene

Sol.

11. Assuming each salt to be completely dissociated which of the following will have highest osmotic pressure-
(A) Decimolar $\text{Al}_2(\text{SO}_4)_3$
(B) Decimolar BaCl_2
(C) Decimolar Na_2SO_4
(D) A solution obtained by mixing equal volumes of (B) and (C) and filtering

Sol.

12. Which one of the following pairs of solution can we expect to be isotonic at the same temperature-
(A) 0.1 M urea and 0.1 M NaCl
(B) 0.1 M urea and 0.2 M MgCl_2
(C) 0.1 M NaCl and 0.1M Na_2SO_4
(D) 0.1 M $\text{Ca}(\text{NO}_3)_2$ and 0.1 M Na_2SO_4

Sol.

- 13.** For a solution containing non-volatile solute, the relative lowering of vapour pressure is 0.2. If the solution contains 5 moles in all, which of the following are true ?

I. Mole fraction of solute in the solution is 0.2
 II. No. of moles of solute in the solution is 0.2
 III. No. of moles of solvent in the solution is 4
 IV. Mole fraction of solvent is 0.2 -
 (A) I, IV (B) II, III
 (C) I, III (D) II, IV

Sol.

- 14.** A complex containing K^+ , Pt (IV) and Cl^- is 100% ionised giving $i = 3$. Thus, complex is
 (A) $K_2 [PtCl_4]$ (B) $K_2 [PtCl_6]$
 (C) $K_3 [PtCl_5]$ (D) $K [PtCl_3]$

Sol.

- 15.** If $pK_a = -\log K_a = 4$, and $K_a = C\alpha^2$ then van't Hoff factor for weak monobasic acid when $C = 0.01$ M is -
 (A) 0.01 (B) 1.02
 (C) 1.10 (D) 1.20

Sol.

- 16.** pH of 1M HA (weak acid) is 2. Hence van't Hoff factor is -
 (A) 1.2 (B) 1.02
 (C) 1.1 (D) 1.01

Sol.

- 17.** In which case van't Hoff factor is maximum
 (A) KCl, 50% ionised
 (B) K_2SO_4 40% ionised
 (C) $FeCl_3$, 30% ionised
 (D) $SnCl_4$, 20% ionised

Sol.

- 18.** If 18 gram of glucose ($C_6H_{12}O_6$) is present in 1000 gram of an aqueous solution of glucose it is said to be -
 (A) 39.2 gram (B) 1.1 molal
 (C) 0.5 molal (D) 0.1 molal

Sol.

- 19.** What is the molarity of H_2SO_4 solution that has a density of 1.84 gm/cc at $35^\circ C$ and contains 98% by weight -
 (A) 4.18 M (B) 8.14 M
 (C) 18.4 M (D) 18 M

Sol.

20. In order to prepare 100 cm^3 of 0.250 M barium chloride solution the amount of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ required will be-
- (A) 0.250 moles
(B) 0.0025 moles
(C) 2.5 moles
(D) 6.1 gram of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$

Sol.

21. 25 mL of 3 M HCl were added to 75 mL of 0.05 M HCl . The molarity of HCl in the resulting solution is approximately-
- (A) 0.055 M (B) 0.35 M
(C) 0.787 M (D) 3.05 M

Sol.

22. 0.2 mole of HCl and 0.1 mole of CaCl_2 were dissolved in water to have 500 ml of solution, the molarity of Cl^- ions is-
- (A) 0.04 M (B) 0.8 M
(C) 0.4 M (D) 0.08 M

Sol.

23. When 5.0 gram of BaCl_2 is dissolved in water to have 10^6 gram of solution. The concentration of solution is-
- (A) 2.5 ppm (B) 5 ppm
(C) 5M (D) 5 gm L^{-1}

Sol.

24. For an ideal binary liquid solution with $P_A^0 > P_B^0$, which relation between X_A (molefraction of A in liquid phase) and Y_A (mole fraction of A in vapour phase) is correct?

- (A) $Y_A < Y_B$ (B) $X_A > X_B$
(C) $\frac{Y_A}{Y_B} > \frac{X_A}{X_B}$ (D) $\frac{Y_A}{Y_B} < \frac{X_A}{X_B}$

Sol.

25. Mole fraction of A vapours above the solution in mixture of A and B ($X_A = 0.4$) will be

[Given : $P_A^0 = 100 \text{ mm Hg}$ and $P_B^0 = 200 \text{ mm Hg}$]

- (A) 0.4 (B) 0.8
(C) 0.25 (D) None of these

Sol.

26. The exact mathematical expression of Raoult's law is

- (A) $\frac{P^0 - P_s}{P^0} = \frac{n}{N}$ (B) $\frac{P^0 - P_s}{P^0} = \frac{N}{n}$
 (C) $\frac{P^0 - P_s}{P_s} = \frac{n}{N}$ (D) $\frac{P^0 - P_s}{P^0} = n \times N$

Sol.

27. A mixture contains 1 mole of volatile liquid A ($P_A^0 = 100$ mm Hg) and 3 moles of volatile liquid B ($P_B^0 = 80$ mmHg). If solution behaves ideally, the total vapour pressure of the distillate is

- (A) 85 mm Hg (B) 85.88 mmHg
 (C) 90 mm Hg (D) 92 mm Hg

Sol.

28. Which of the following aqueous solution will show maximum vapour pressure at 300 K?

- (A) 1 M NaCl (B) 1 M CaCl_2
 (C) 1 M AlCl_3 (D) 1 M $\text{C}_{12}\text{H}_{22}\text{O}_{11}$

Sol.

29. The Van't Hoff factor for a dilute aqueous solution of glucose is

- (A) zero (B) 1.0 (C) 1.5 (D) 2.0

Sol.

30. The correct relationship between the boiling points of very dilute solution of AlCl_3 ($T_1\text{K}$) and CaCl_2 ($T_2\text{K}$) having the same molar concentration is

- (A) $T_1 = T_2$ (B) $T_1 > T_2$ (C) $T_2 > T_1$ (D) $T_2 \leq T_1$

Sol.

31. A 0.001 molal solution of a complex $[\text{MA}_8]$ in water has the freezing point of -0.0054°C . Assuming 100% ionization of the complex salt and K_f for $\text{H}_2\text{O} = 1.86 \text{ K m}^{-1}$, write the correct representation for the complex

- (A) $[\text{MA}_8]$ (B) $[\text{MA}_7]\text{A}$ (C) $[\text{MA}_6]\text{A}_2$ (D) $[\text{MA}_5]\text{A}_3$

Sol.

32. The vapour pressure of a solution of a non-volatile electrolyte B in a solvent A is 95% of the vapour pressure of the solvent at the same temperature. If the molecular weight of the solvent is 0.3 times the molecular weight of solute, the weight ratio of the solvent and solute are

- (A) 0.15 (B) 5.7 (C) 0.2 (D) 4.0

Sol.

33. At a given temperature, total vapour pressure in Torr of a mixture of volatile components A and B is given by

$$P_{\text{Total}} = 120 - 75 X_B$$

hence, vapour pressure of pure A and B respectively (in Torr) are

- (A) 120, 75 (B) 120, 195 (C) 120, 45 (D) 75, 45

Sol.

34. Assuming each salt to be 90% dissociated, which of the following will have highest boiling point?

- (A) Decimolar $\text{Al}_2(\text{SO}_4)_3$
(B) Decimolar BaCl_2
(C) Decimolar Na_2SO_4
(D) A solution obtained by mixing equal volumes of (B) and (C)

Sol.

35. The vapour pressure of a solvent decreased by 10 mm of Hg when a non-volatile solute was added to the solvent. The mole fraction of solute in solution is 0.2, what would be mole fraction of the solvent if decrease in vapour pressure is 20 mm of Hg.

- (A) 0.2 (B) 0.4 (C) 0.6 (D) 0.8

Sol.

37. What will be the molecular weight of CaCl_2 determined in its aq. solution experimentally from depression of freezing point?

- (A) 111 (B) < 111
(C) > 111 (D) data insufficient

Sol.

36. Elevation of boiling point of 1 molar aqueous glucose solution (density = 1.2 g/ml) is

- (A) K_b (B) $1.20 K_b$ (C) $1.02 K_b$ (D) $0.98 K_b$

Sol.

38. 1.0 molal aqueous solution of an electrolyte A_2B_3 is 60% ionised. The boiling point of the solution at 1 atm is ($K_{b(\text{H}_2\text{O})} = 0.52 \text{ K kg mol}^{-1}$)

- (A) 274.76 K (B) 377 K
(C) 376.4 K (D) 374.76 K

Sol.

39. Which of the following plots represents an ideal binary mixture?

(A) Plot of $P_{\text{total}} v/s 1/X_B$ is linear (X_B = mole fraction of 'B' in liquid phase)

(B) Plot of $P_{\text{total}} v/s Y_A$ is linear (Y_B = mole fraction of 'A' in vapour phase)

(C) Plot of $\frac{1}{P_{\text{total}}} v/s Y_A$ is linear

(D) Plot of $\frac{1}{P_{\text{total}}} v/s Y_B$ is non linear

Sol.

41. Two liquids A & B form an ideal solution. What is the vapour pressure of solution containing 2 moles of A and 3 moles of B at 300 K? [Given : At 300 K, Vapour pr. of pure liquid A (P_A^0) = 100 torr, Vapour pr. of

pure liquid B (P_B^0) = 300 torr]

(A) 200 torr

(B) 140 torr

(C) 180 torr

(D) None of these

Sol.

40. Pressure over ideal binary liquid mixture containing 10 moles each of liquid A and B is gradually decreased isothermally. If $P_A^0 = 200$ mm Hg and $P_B^0 = 100$ mm Hg, find the pressure at which half of the liquid is converted into vapour.

(A) 150 mm Hg

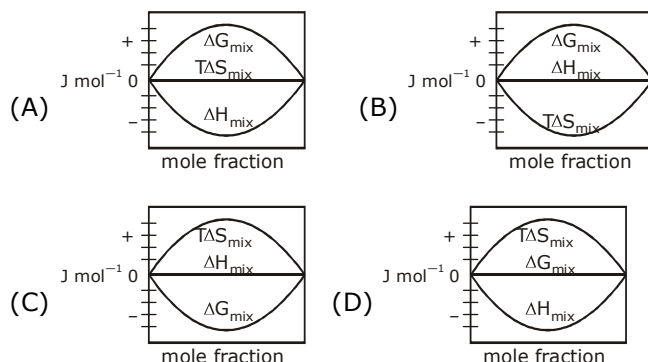
(B) 166.5 mm Hg

(C) 133 mm Hg

(D) 141.4 mm Hg

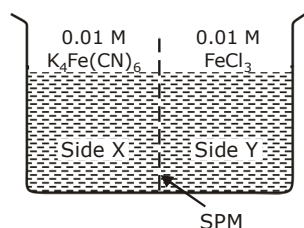
Sol.

42. Which of the following represents correctly the changes in the changes in thermodynamic properties during the formation of 1 mol of an ideal binary solution



Sol.

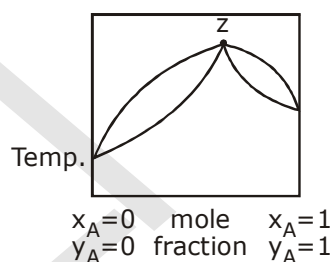
43. FeCl_3 on reaction with $\text{K}_4[\text{Fe}(\text{CN})_6]$ in aqueous solution gives blue colour. These are separated by a semipermeable membrane AB as shown. Due to osmosis there is



- (A) Blue colour formation in side X.
- (B) Blue colour formation in side Y.
- (C) Blue colour formation in both of the sides X and Y.
- (D) No blue colour formation.

Sol.

44. A liquid mixture having composition corresponding to point z in the figure shown is subjected to distillation at constant pressure. Which of the following statement is correct about the process



- (A) The composition of distillate differs from the mixture
- (B) The boiling point goes on changing
- (C) The mixture has highest vapour pressure than for any other composition
- (D) Composition of an azeotrope alters on changing the external pressure.

Sol.

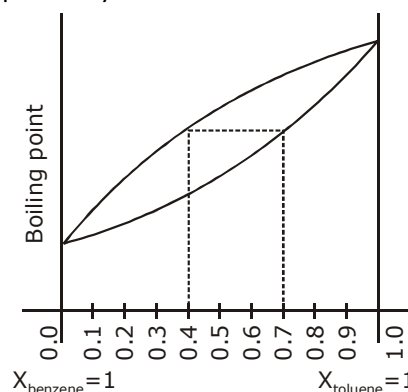
45. The vapour pressure of a saturated solution of sparingly soluble salt(XCl_3) was 17.20 mm Hg at 27°C . If the vapour pressure of pure H_2O is 17.25 mm Hg at 300 K, what is the solubility of sparingly soluble salt XCl_3 in mole/Litre.

- (A) 4.04×10^{-2} (B) 8.08×10^{-2}
(C) 2.02×10^{-2} (D) 4.04×10^{-3}

Sol.

47. the following graph represents variation of boiling point with composition of liquid and vapours of binary liquid mixture. The graph is plotted at constant pressure.

Which of the following statement is **incorrect**. Here X & Y stands for mole fraction in liquid and vapour phase respectively



- (A) $X_{\text{benzene}} = 0.5$ and $Y_{\text{toluene}} = 0.2$
(B) $X_{\text{toluene}} = 0.3$ and $Y_{\text{benzene}} = 0.6$
(C) $X_{\text{benzene}} = 0.3$ and $Y_{\text{toluene}} = 0.4$
(D) if $X_{\text{benzene}} = 0.7$ then $Y_{\text{toluene}} < 0.3$

Sol.

46. At 300 K, the vapour pressure of an ideal solution containing 3 mole of A and 2 mole of B is 600 torr. At the same temperature, if 1.5 mole of A & 0.5 mole of C(non-volatile) are added to this solution the vapour pressure of solution increases by 30 torr. What is the value of P_B^0 ?

- (A) 940 (B) 405 (C) 90 (D) None of these

Sol.

48. The freezing point depression of a 0.1 M aq. solution of weak acid (HX) is -0.20°C .

What is the value of equilibrium constant for the reaction?



[Given : K_f for water $1.8 \text{ kg mol}^{-1} \text{ K}$. & Molality = Molarity]

- (A) 1.46×10^{-4} (B) 1.35×10^{-3}
(C) 1.21×10^{-2} (D) 1.35×10^{-4}

Sol.

50. The vapour pressure of an aqueous solution is found to be 750 torr at certain temperature 'T'. If 'T' is the temperature at which pure water boils under atmospheric pressure and same solution show elevation in boiling point $\Delta T_b = 1.04 \text{ K}$, find the atmospheric pressure. ($K_b = 0.52 \text{ K kg mol}^{-1}$)

- (A) 777 (B) 779 (C) 782 (D) 746

Sol.

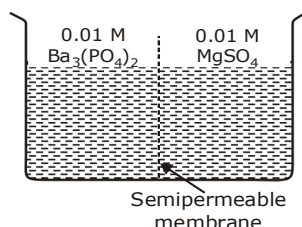
49. The van't Hoff factor for 0.1 M $\text{Ba}(\text{NO}_3)_2$ solution is 2.74. The degree of dissociation is

- (A) 91.3% (B) 87% (C) 100% (D) 74%

Sol.

Exercise - II**(One or more than one option correct)**

1. Study the following figure and choose the correct options from the given below (assuming both dissociate completely).



- (A) There will be no movement from any solution across the membrane
- (B) Osmotic pressure of 0.1 M $\text{Ba}_3(\text{PO}_4)_2$ will be higher than 0.1 M MgSO_4 solution
- (C) There will be flow from right side of S.P.M. to that of left
- (D) White precipitate (BaSO_4) will not be formed in right side of the S.P.M.

Sol.

2. When CuSO_4 is dissolved in NH_4OH solution then the correct statement is

- (A) Freezing point of solution is raised
- (B) Boiling point of solution is lowered
- (C) Freezing point of solution is lowered
- (D) Boiling point of solution is raised

Sol.

3. The example of negative deviation is

- (A) HCl & H_2O
- (B) $\text{C}_2\text{H}_5\text{OH}$ & H_2O
- (C) CHCl_3 & CH_3COCH_3
- (D) C_6H_6 & $\text{C}_6\text{H}_5\text{CH}_3$

Sol.

4. acetone and carbon disulphide form binary liquid solution showing positive deviation from Raoult law. The normal boiling point (T_b) of pure acetone is less than that of pure CS_2 . Pick out the **incorrect** statements among the following.

- (A) Boiling temperature of mixture is always less than boiling temperature of acetone.
- (B) Boiling temperature Azeotropic mixture is always less than boiling temperature of pure CS_2
- (C) When a small amount CS_2 (less volatile component) is added to excess of acetone boiling point of resulting mixture increases.
- (D) A mixture of CS_2 and CH_3COCH_3 can be completely separated by simple fractional distillation.

Sol.

Passage

Vapour pressure of a solvent is the pressure exerted by vapours when they are in equilibrium with its solvent at that temperature. The vapour pressure of solvent is dependent on nature of solvent, temperature, addition of non-volatile solute as well as nature of solute to dissociate or associate. The vapour pressure of a mixture obtained by mixing two volatile liquids is given by $P_M = P_A^0 \cdot X_A + P_B^0 \cdot X_B$ where P_A^0 and P_B^0 are vapour pressures of pure components A and B and X_A , X_B are their mole fraction in mixture. For solute-solvent system, the relation becomes $P_M = P_A^0 \cdot X_A$ where B is non-volatile solute.

5. The vapour pressure of benzene and its solution with a non-electrolyte are 640 and 600 mm respectively. The molality of the solution is -

- (A) 0.80 (B) 0.86
(C) 0.90 (D) 0.95

Sol.

6. A mixture of two volatile liquids A and B for 1 and 3 moles respectively has a V.P. of 300 mm at 27°C. If one mole of A is further added to this solution, the vapour pressure becomes 290 mm at 27°C. The vapour pressure of pure A is -

- (A) 250 mm (B) 316 mm
(C) 220 mm (D) 270 mm

Sol.

7. The amount of solute (mol. wt. 60) required to dissolve in 180 g of water to reduce the vapour pressure to 4/5 of the pure water -

- (A) 120 g (B) 150 g
(C) 200 g (D) 60 g

Sol.

Assertion & Reasoning type questions

Each of the questions given below consists of Statement - I and Statement - II. Use the following Key to choose the appropriate answer.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

8. Statement - I. Addition of a non-volatile solute causes a depression in vapour pressure.

Statement - II. Vapour pressure of a solution is directly proportional to mole fraction of solvent.

Sol.

9. Statement - I. 0.02 m solutions of urea and sucrose will freeze at same temperature.

Statement - II. Freezing point of a solution is inversely proportional to the concentration of solution.

Sol.

10. Statement - I. For isotonic solutions $C_1 = C_2$

Statement - II. For isotonic solutions $\pi_1 = \pi_2$

Sol.

11. Statement - I. Benzene-toluene mixture forms ideal solution.

Statement - II. Components with structural similarity forms ideal solution in general.

Sol.

12. Statement - I. Dissolution of sulphuric acid in water gives a solution which shows negative deviation.

Statement - II. The solutions which have same vapour pressure at a given temperature are called isotonic solutions.

Sol.

13. Statement - I. Greater the molal depression constant of the solvent used less in the freezing point of the solution.

Statement - II. Depression in freezing point depends upon the nature of the solvent.

Sol.

14. Statement - I. Vant Hoff factor for electrolytes is always greater than unity.

Statement - II. The no. of particles increases in solution due to electrolytic dissociation.

Sol.

15. Statement - I. The vapour pressure of 0.1 M sugar solution is more than that of 0.1 M potassium chloride solution.

Statement - II. Lowering of vapour pressure is directly proportional to the no. of species present in the solution.

Sol.

16. Statement - I. Blood cells are isotonic with 0.16 M NaCl solution.

Statement - II. Cell wall of blood cells acts as semi-permeable membrane.

Sol.

17. Statement - I. Molarity of the solution changes with temperature.

Statement - II. volume is function of Temperature.

Sol.

18. Statement-1 : The freezing of water is an endothermic process.

Statement-2 : Heat must be removed from the water to make it freeze.

Sol.

19. Statement-1 : Addition of ethylene glycol (non-volatile) to water lowers the freezing point of water hence used as antifreeze.

Statement-2 : Addition of any substance to water lowers its freezing point of water.

Sol.

Match the following columns :

20. Column I

- (A) Ideal solution
- (B) Solutions showing positive deviations
- (C) Solutions showing negative deviations

Column II

- (P) Solute-solvent interactions are weaker than solute-solute
- (Q) Solute-solvent interactions are similar to solute-solute
- (R) Solute-solvent interactions are stronger than solute-solute interactions

Sol.

21. Column I

- (A) $\Delta H_{\text{mix}} = 0$
- (B) $\Delta T_f/\text{molality}$
- (C) $(n - 1) \alpha + 1$
- (D) $\pi_1 = \pi_2$
- (E) $\Delta P/P^\circ$

Column II

- (P) Isotonic solutions
- (Q) Mole fraction of solute
- (R) Ideal solution
- (S) Van't Hoff factor for electrolyte
- (T) Molal depression constant

Sol.

22. When mercuric iodide is added to the aqueous solution of potassium iodide, the - **[IIT-1987]**

- (A) freezing point is raised
- (B) freezing point is lowered
- (C) freezing point does not change
- (D) boiling point does not change

Sol.

23. A sugar syrup of weight 214.2 grams contains 34.2 grams of sugar. The molal concentration is- **[IIT-1988]**

- (A) 0.55
- (B) 5.5
- (C) 55
- (D) 0.1

Sol.

24. The vapour pressure of benzene at a certain temp. is 640 mm Hg. A non-volatile-non-electrolyte and weighing 2.175 g is added to 39.0 g of benzene. The vapour pressure of the solution is 600 mm Hg. What is the molecular weight of the solid substance ? [IIT-1990]

(A) 6.96 (B) 65.3
(C) 63.8 (D) none of these

Sol.

25. The vapour pressure of solution containing 5 g of non-electrolyte in 90g of water at a particular temperature is 2985 Nm⁻². The vapour pressure of pure water at that temperature is 3000 Nm⁻². The molecular weight of the solute is - [IIT-1993]

(A) 180 (B) 90
(C) 270 (D) 200

Sol.

26. Increasing the temperature of an aqueous solution will cause - [IIT-1993]

(A) decrease in molality
(B) decrease in molarity
(C) decrease in mole fraction
(D) decrease in % (w/w)

Sol.

27. The molecular weight of benzoic acid in benzene as determined by depressing in freezing point method corresponds to - [IIT-1996]

(A) ionization of benzoic acid
(B) dimerization of benzoic acid
(C) trimerization of benzoic acid
(D) solvation of benzoic acid

Sol.

28. Azeotropes are [IIT-1996]

(A) liquid mixtures which distil unchanged in composition
(B) liquids which can mix with each other in all proportions
(C) solids which form solid solutions of definite composition
(D) gases which can be separated

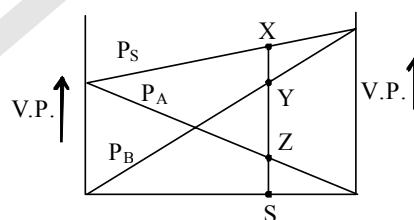
Sol.

29. 0.2 molal acid HX is 20% ionised in solution $K_f = 1.86 \text{ K molality}^{-1}$. The freezing point of the solution is - [IIT-1997]

(A) - 0.45 (B) - 0.90
(C) - 0.30 (D) -0.53

Sol.

30. Consider following vapour pressure composition graph. Hence-



(A) V.P. of A = SZ
(B) V.P. of B = ZY
(C) V.P. of B = SY
(D) V.P. of solution at X = SZ + SY

Sol.

Exercise - III**Subjective Level-I**

1. At 25°C, the vapour pressure of methyl alcohol is 96.0 torr. What is the mole fraction of CH_3OH in a solution in which the (partial) vapour pressure of CH_3OH is 23.0 torr at 25°C?

Sol.

2. The vapour pressure of pure liquid solvent A is 0.80 atm. When a non-volatile substance B is added to the solvent, its vapour pressure drops to 0.60 atm. what is the mole fraction of the component B in the solution ?

Sol.

3. The vapour pressure of pure water at 26°C is 25.21 torr. What is the vapour pressure of a solution which contains 20.0 glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, in 70 g water?

Sol.

4. The vapour pressure of pure water at 25°C is 23.76 torr. The vapour pressure of a solution containing 5.40 g of a nonvolatile substance in 90.0 g water is 23.32 torr. Compute the molecular weight of the solute.

Sol.

Raoult's law in combination with Dalton's law of P.P. and V.P. lowering

5. The vapour pressure of ethanol and methanol are 44.5 mm and 88.7 mm Hg respectively. An ideal solution is prepared at the same temperature by mixing 60 g of ethanol with 40 g of methanol. Calculate total vapour pressure of the solution.

Sol.

6. Calculate the mole fraction of toluene in the vapour phase which is in equilibrium with a solution of benzene and toluene having a mole fraction of toluene 0.5. The vapour pressure of pure benzene is 119 torr, that of toluene is 37 torr at the same temperature.

Sol.

7. What is the composition of the vapour which is in equilibrium at 30°C with a benzene-toluene solution with a mole fraction of benzene of 0.40 ? With a mole fraction of benzene of 0.60?

$$P_b^0 = 119 \text{ torr and } P_t^0 = 37 \text{ torr}$$

Sol.

8. At 90°C, the vapour pressure of toluene is 400 torr and that of σ -xylene is 150 torr. What is the composition of the liquid mixture that boils at 90°C, when the pressure is 0.50 atm? What is the composition of vapour produced?

Sol.

9. Two liquids A and B form an ideal solution at temperature T. When the total vapour pressure above the solution is 400 torr, the mole fraction of A in the vapour phase is 0.40 and in the liquid phase 0.75. What are the vapour pressure of pure A and pure B at temperature T?

Sol.

10. Calculate the relative lowering in vapour pressure if 100 g of a nonvolatile solute (mol. wt. 100) are dissolved in 432 g water.

Sol.

Sol.

11. What weight of the non-volatile solute urea needs to be dissolved in 100 g of water, in order to decrease the vapour pressure of water by 25% ? What will be the molality of the solution

Sol.

13. The vapour pressure of pure benzene at 25°C is 639.7 mm of Hg and the vapour pressure of a solution of a solute in C_6H_6 at the same temperature is 631.7 mm of Hg. Calculate molality of solution.

Sol.

12. The vapour pressure of an aqueous solution of glucose is 750 mm Hg at 373 K. Calculate molality and mole fraction of solute.

14. The vapour pressure of pure benzene at a certain temperature is 640 mm of Hg. A nonvolatile nonelectrolyte solid weighing 2.175 g is added to 39.0 of benzene. The vapour pressure of the solution is 600 mm of Hg. What is molecular weight of solid substance?

Sol.

Sol.

15. The vapour pressure of water is 17.54 mm Hg at 293 K. Calculate vapour pressure of 0.5 molal solution of a solute in it.

Sol.

Boiling point elevation and freezing point depression

17. When 10.6 g of a nonvolatile substance is dissolved in 740 g of ether, its boiling point is raised 0.284°C. What is the molecular weight of the substance? Molal boiling point constant for ether is 2.11°C kg/mol.

Sol.

16. Benzene and toluene form two ideal solution A and B at 313 K. Solution A (total pressure P_A) contains equal mole of toluene and benzene. Solution B contains equal masses of both (total pressure P_B). The vapour pressure of benzene and toluene are 160 and 60 mm Hg respectively at 313 K. Calculate the value of P_A/P_B .

18. A solution containing 3.24 g of a nonvolatile nonelectrolyte and 200 g of water boils at 100.130°C at 1 atm. What is the molecular weight of the solute? (K_b for water 0.513°C/m)

Sol.

19. The molecular weight of an organic compound is 58.0 g/mol. compute the boiling point of a solution containing 24.0 g of the solute and 600 g of water, when the barometric pressure is such that pure water boils at 99.725°C. (K_b for water 0.513°C/m)

Sol.

20. An aqueous solution of a nonvolatile solute boils at 100.17°C. At water temperature will this solution freeze? [K_f for water 1.86°C/m]

Sol.

21. Pure benzene freeze at 5.45°C. A solution containing 7.24 g of $C_2H_2Cl_4$ in 115.3 g of benzene was observed to freeze at 3.55°C. What is the molal freezing point constant of benzene?

Sol.

22. A solution containing 6.35 g of a nonelectrolyte dissolved in 500 g of water freezes at -0.465°C . Determine the molecular weight of the solute. [K_f for water 1.86°C/m]

Sol.

23. The freezing point of a solution containing 2.40 g of a compound in 60.0 g of benzene is 0.10°C lower than that of pure benzene. What is the molecular weight of the compound? (K_f is 5.12°C/m for benzene)

Sol.

25. Calculate the molal elevation constant, K_b for water and the boiling of 0.1 molal urea solution. Latent heat of vaporisation of water is $9.72 \text{ kcal mol}^{-1}$ at 373.15 K .

Sol.

24. The elements X and Y form compounds having molecular formula XY_2 and XY_4 . When dissolved in 20 gm of benzene, 1 gm XY_2 lowers the freezing point by 2.3° , whereas 1 gm of XY_4 lowers the freezing point by 1.3°C . The molal depression constant for benzene is 5.1. Calculate the atomic masses of X and Y.

Sol.

26. Calculate the amount of ice that will separate out of cooling a solution containing 50 g of ethylene glycol in 200 g water to -9.3°C . (K_f for water = $1.86 \text{ K mol}^{-1} \text{ kg}$)

Sol.

27. A solution of 0.643 g of an organic compound in 50 ml of benzene (density: 0.879 g/mol) lowers its freezing point from 5.51°C to 5.03°C. If K_f for benzene is 5.12 K, calculate the molecular weight of the compound.

Sol.

28. The cryoscopic constant for acetic acid is 3.6 K kg/mol. A solution of 1 g of a hydrocarbon in 100 g of acetic acid freezes at 16.14°C instead of the usual 16.60°C. The hydrocarbon contains 92.3% carbon. What is the molecular formula?

Sol.

Osmotic pressure

29. Find the freezing point of a glucose solution whose osmotic pressure at 25°C is found to be 30 atm $K_f(\text{water}) = 1.86 \text{ kg. mol}^{-1} \cdot \text{K}$.

Sol.

30. At 300 K, two solution of glucose in water of concentration 0.01 M and 0.001 M are separated by semipermeable membrane. Pressure needs to be applied on which solution, to prevent osmosis? calculate the magnitude of this applied pressure.

Sol.

31. At 10°C, the osmotic pressure of urea solution is 500 mm. The solution is diluted and the temperature is raised to 25°C, when the osmotic pressure is found to be 105.3 mm. Determine extent of dilution.

Sol.

33. What would be the osmotic pressure at 17°C of an aqueous solution containing 1.75 g of sucrose ($C_{12}H_{22}O_{11}$) per 150 cm³ of solution?

Sol.

32. The osmotic pressure of blood is 7.65 atm at 37°C. How much glucose should be used per L for an intravenous injection that is to have the same osmotic pressure as blood?

Sol.

34. A 250 mL water solution containing 48.0 g of sucrose, $C_{12}H_{22}O_{11}$, at 300 K is separated from pure water by means of a semipermeable membrane. What pressure must be applied above the solution in order to just prevent osmosis?

Sol.

35. A solution of crab hemocyanin, a pigmented protein extracted from crabs, was prepared by dissolving 0.750 g in 125 cm³ of an aqueous medium. At 4°C an osmotic pressure rise of 2.6 mm of the solution was observed. The solution had a density of 1.00g/cm³. Determine the molecular weight of the protein.

Sol.

36. The osmotic pressure of a solution of a synthetic polyisobutylene in benzene was determined at 25°C. A sample containing 0.20 g of solute/100cm³ of solution developed a rise of 2.4 mm at osmotic equilibrium. The density of the solution was 0.88g/cm³. What is the molecular weight of the polyisobutylene?

Sol.

37. A 5% solution (w/v) of cane-sugar (Mol. weight = 342) is isotonic with 0.877% (w/v) of urea solution. Find molecular weight of urea.

Sol.

38. 10 gm of solute A and 20 gm of solute B are both dissolved in 500 ml water. The solution has the same osmotic pressure as 6.67 gm of A and 30 g of B dissolved in the same amount of water at the same temperature. What is the ratio of molar masses of A and B?

Sol.

Van't Hoff factor & colligative properties

39. A storage battery contains a solution of H_2SO_4 38% by weight. What will be the Van't Hoff factor if the $\Delta T_{f(\text{experiment})}$ is 29.08. [Given $K_f = 1.86 \text{ mol}^{-1} \text{ Kg}$]

Sol.

41. 2.0 g of benzoic acid dissolved in 25.0 g of benzene shows a depression in freezing point equal to 1.62 K. Molal depression constant (K_f) of benzene is $4.9 \text{ K kg. mol}^{-1}$. What is the percentage association of the acid?

Sol.

40. A certain mass of a substance, when, dissolved in 100 g C_6H_6 , lowers the freezing point by 1.28°C . The same mass of solute dissolved in 100 g water lowers the freezing point by 1.40°C . If the substance has normal molecular weight in benzene and is completely ionized in water, into how many ions does it dissociate in water? K_f for H_2O and C_6H_6 are 1.86 and $5.12 \text{ K kg mol}^{-1}$

Sol.

42. A decimolar solution of potassium ferrocyanide is 50% dissociated at 300 K. Calculate the osmotic pressure of the solution. ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)

Sol.

43. The freezing point of a solution containing 0.2 g of acetic acid in 20.0 g of benzene is lowered by 0.45°C . Calculate the degree of association of acetic acid in benzene. (K_f for benzene = $5.12 \text{ K mol}^{-1} \text{ kg}$)

Sol.

44. 0.85% (w/v) aqueous solution of NaNO_3 is apparently 90% dissociated at 27°C . Calculate its osmotic pressure. ($R = 0.082 \text{ l atm K}^{-1} \text{ mol}^{-1}$)

Sol.

45. A 1.2% solution (w/v) of NaCl is isotonic with 7.2% solution (w/v) of glucose. Calculate degree of ionization and Van't Hoff factor of NaCl .

Sol.

46. An aqueous solution containing 288 gm of a non-volatile compound having the stoichiometric composition $\text{C}_x\text{H}_{2x}\text{O}_x$ in 90 gm water boils at 101.24°C at 1.00 atmospheric pressure. What is the molecular formula?

$$K_b(\text{H}_2\text{O}) = 0.512 \text{ K mol}^{-1} \text{ kg}$$

$$T_b(\text{H}_2\text{O}) = 100^{\circ}\text{C}$$

Sol.

47. The addition of 3 gm of substance to 100 gm CCl_4 ($M = 154 \text{ gm mol}^{-1}$) raises the boiling point of CCl_4 by 0.60°C of $K_b(\text{CCl}_4)$ is $5.03 \text{ kg mol}^{-1} \text{ K}$. Calculate

- (a) The freezing point depression
- (b) The relative lowering of vapour pressure
- (c) The osmotic pressure at 298 K
- (d) The molar mass of the substance

Given $K_f(\text{CCl}_4) = 31.8 \text{ kg mol}^{-1} \text{ K}$ and ρ (density) of solution = 1.64 gm/cm^3

Sol.

48. Vapour pressure of C_6H_6 and C_7H_8 mixture at 50°C is given by $P(\text{mm Hg}) = 180 X_B + 90$, where X_B is the mole fraction of C_6H_6 . A solution is prepared by mixing 936 g benzene and 736 g toluene and if the vapours over this solution are removed and condensed into liquid and again brought to the temperature of 50°C , what would be mole fraction of C_6H_6 in the vapour state?

Sol.

49. At 100°C , benzene & toluene have vapour pressure of 1375 & 558 Torr respectively. Assuming these two form an ideal binary solution, calculate the composition of the solution that boils at 1 atm & 100°C . What is the composition of vapour issuing at these conditions?

Sol.

50. Calculate the boiling point of solution containing 0.61 g of benzoic acid in 50 g of carbon disulphide assuming 84% dimerization of the acid. The boiling point and K_b of CS_2 are 46.2°C and $2.3 \text{ K kg mol}^{-1}$, respectively.

Sol.

51. The molar volume of liquid benzene (density = 0.877 g ml^{-1}) increases by a factor of 2750 as it vaporizes at 20°C and that of liquid toluene (density = 0.867 g ml^{-1}) increases by a factor of 7720 at 20°C . Solution of benzene & toluene has a vapour pressure of 46.0 torr. Find the mole fraction of benzene in the vapour above the solution.

Sol.

52. Dry air was drawn through bulbs containing a solution of 40 grams of urea in 300 grams of water, then through bulbs containing pure water at the same temperature and finally through a tube in which pumice moistened with strong H_2SO_4 was kept. The water bulbs lost 0.0870 grams and the sulphuric acid tube gained 2.036 grams. Calculate the molecular weight of urea.

Sol.

53. The vapour pressure of two pure liquids, A and B that form an ideal solution are 300 and 800 torr respectively, at temperature T. A mixture of the vapour of A and B for which the mole fraction of A is 0.25 is slowly compressed at temperature T. Calculate

- (a) The composition of the first drop of the condensate,
- (b) The total pressure when this drop is formed,
- (c) The composition of the solution whose normal boiling point is T,
- (d) The pressure when only the last bubble of vapour remains, and
- (e) The composition of the last bubble.

Sol.

54. The degree of dissociation of $\text{Ca}(\text{NO}_3)_2$ in a dilute aqueous solution containing 7 gm of the salt per 100 gm of water at 100°C is 70%. If the vapour pressure of water at 100°C is 760 mm. Calculate the vapour pressure of the solution.

Sol.

55. A 10% (w/w) solution of cane sugar has undergone partial inversion according to the reaction:

Sucrose + Water \rightarrow Glucose + Fructose. If the boiling point of solution is 100.27°C .

- (a) What is the average mass of the dissolved materials?
- (b) What fraction of the sugar has inverted?
 $K_b(\text{H}_2\text{O}) = 0.512 \text{ K mol}^{-1} \text{ kg}$

Sol.

56. 1.5 g of a monobasic acid when dissolved in 150 g of water lowers the freezing point by 0.165°C . 0.5 g of the same acid when titrated, after dissolution in water, requires 37.5 ml of N/10 alkali. Calculate the degree of dissociation of the acid (K_f for water = $1.86^{\circ}\text{C mol}^{-1}$).

Sol.

57. Sea water is found to contain 5.85% NaCl and 9.50 % MgCl_2 by weight of solution. Calculate its normal boiling point assuming 80% ionisation for NaCl and 50% ionisation of MgCl_2 [$K_b(\text{H}_2\text{O}) = 0.51 \text{ kg mol}^{-1}\text{K}$].

Sol.

58. The latent heat of fusion of ice is 80 calories per gram at 0°C . What is the freezing point of a solution of KCl in water containing 7.45 grams of solute in 500 grams of water, assuming that the salt is dissociated to the extent of 95% ?

Sol.

59. A complex is represented as $\text{CoCl}_3 \cdot x\text{NH}_3$. It's 0.1 molal solution in aq. solution shows $\Delta T_f = 0.558^{\circ}\text{C}$. K_f for H_2O is $1.86 \text{ K mol}^{-1} \text{ kg}$. Assuming 100% ionisation of complex and coordination no. of Co is six, calculate formula of complex.

Sol.

60. At 25°C , 1 mol of A having a vapor pressure of 100 torr and 1 mol of B having a vapour pressure of 300 torr were mixed. The vapour at equilibrium is removed, condensed and the condensate is heated back to 25°C . the vapours now formed are again removed, recondensed and analyzed. What is the mole fraction of A in this condensate?

Sol.

61. Phenol associates in benzene to a certain extent to form a dimer. A solution containing 20×10^{-3} kg phenol in 1 kg of benzene has its freezing point depressed by 0.69 K. Calculate the fraction of phenol that has dimerised. K_f for benzene = $5.12 \text{ kg mol}^{-1} \text{ K}$.

Sol.

62. 30 ml of CH_3OH ($d = 0.7980 \text{ gm cm}^{-3}$) and 70 ml of H_2O ($d = 0.9984 \text{ gm cm}^{-3}$) are mixed at 25°C to form a solution of density $0.9575 \text{ gm cm}^{-3}$. Calculate the freezing point of the solution. $K_f(\text{H}_2\text{O})$ is $1.86 \text{ kg mol}^{-1} \text{ K}$. Also calculate its molarity.

Sol.

63. When the mixture of two immiscible liquids (water and nitrobenzene) boils at 372 K and the vapour pressure at this temperature are 97.7 kPa (H_2O) and 3.6 kPa ($\text{C}_6\text{H}_5\text{NO}_2$). Calculate the weight% of nitrobenzene in the vapour.

Sol.

64. A very dilute saturated solution of a sparingly soluble salt A_3B_4 has a vapour pressure of 20 mm of Hg at temperature T, while pure water exerts a pressure 20.0126 mm Hg at the same temperature. Calculate the solubility product constant of A_3B_4 at the same temperature.

Sol.

65. If the apparent degree of ionization of KCl ($KCl = 74.5 \text{ gm mol}^{-1}$) in water at 290 K is 0.86. Calculate the mass of KCl which must be made up to 1 dm^3 of aqueous solution to the same osmotic pressure as the 4.0% solution of glucose at that temperature.

Sol.

66. An ideal solution was prepared by dissolving some amount of cane sugar (non-volatile) in 0.9 moles of water. The solution was then cooled just below its freezing temperature (271 K), where some ice get separated out. the remaining aqueous solution registered a vapour pressure of 700 torr at 373 K. Calculate the mass of ice separated out, if the molar heat of fusion of water is 6 kJ.

Sol.

67. The specific conductivity of a 0.5 M aq. solution of monobasic acid HA at 27°C is 0.006 S cm⁻¹. It's molar conductivity at infinite dilution is 200 S cm² mol⁻¹.

Calculate osmotic pressure (in atm) of 0.5 M HA (aq) solution at 27°C

$$\text{Given } R = 0.08 \frac{\text{atmL}}{\text{mol K}}$$

Sol.

68. The freezing point of 0.02 mol fraction solution of acetic acid (A) in benzene (B) is 277.4 K. Acetic acid exists partly as a dimer $2A = A_2$. Calculate equilibrium constant for the dimerisation. Freezing point of benzene is 278.4 K and its heat of fusion ΔH_f is 10.042 kJ mol⁻¹.

Sol.

69. Tritium, T (an isotope of H) combines with fluorine to form weak acid TF, which ionizes to give T⁺. Tritium is radioactive and is a β -emitter. A freshly prepared aqueous solution of TF has pT (equivalent of pH) of 1.5 and freezes at -0.372°C. If 600 ml of freshly prepared solution were allowed to stand for 24.8 years. Calculate (i) ionization constant of TF. (ii) Number of β -particles emitted.

(Given K_f for water = 1.86 kg mol K⁻¹, $t_{1/2}$ for tritium = 12.4 years)

Sol.

LEVEL – IV

PREVIOUS YEARS

LEVEL – I

JEE MAIN

1. Which of the following concentration factor is affected by change in temperature ? [AIEEE-2002]

- (A) Molarity (B) Molality
(C) Mol fraction (D) Weight fraction

Sol.

2. For an aqueous solution, freezing point is -0.186°C . Boiling point of the same solution is

($K_f = 1.86^{\circ}\text{K mol}^{-1}\text{kg}$) and

($K_b = 0.512^{\circ}\text{K mol}^{-1}\text{kg}$) [AIEEE-2002]

- (A) 0.186° (B) 100.0512°
(C) 1.86° (D) 5.12°

Sol.

3. In a mixture of A and B, components show negative deviation when – [AIEEE-2002]

- (A) A – B interaction is stronger than A – A and B – B interaction
(B) A – B interaction is weaker than A – A and B – B interaction
(C) $\Delta V_{\text{mix}} > 0$, $\Delta S_{\text{mix}} > 0$
(D) $\Delta V_{\text{mix}} = 0$, $\Delta S_{\text{mix}} > 0$

Sol.

4. A pressure cooker reduces cooking time for food because – [AIEEE-2003]

- (A) The higher pressure inside the cooker crushes the food material
(B) Cooking involves chemical changes helped by a rise in temperature
(C) Heat is more evenly distributed in the cooking space
(D) Boiling point of water involved in cooking is increased

Sol.

5. If liquids A and B form an ideal solution –

[AIEEE-2003]

- (A) The free energy of mixing is zero
(B) The free energy as well as the entropy of mixing are each zero
(C) The enthalpy of mixing is zero
(D) The entropy of mixing is zero

Sol.

6. In a 0.2 molal aqueous solution of a weak acid HX the degree of ionization is 0.3. Taking k_f for water as 1.85, the freezing point of the solution will be nearest to – [AIEEE-2003]

- (A) -0.260°C (B) $+0.480^{\circ}\text{C}$
(C) -0.480°C (D) -0.360°C

Sol.

7. If liquid A and B form ideal solution, than :

[AIEEE-2003]

- (A) $\Delta G_{\text{mix}} = 0$
(B) $\Delta H_{\text{mixing}} = 0$
(C) $\Delta G_{\text{mix}} = 0, \Delta S_{\text{mix}} = 0$
(D) $\Delta S_{\text{mix}} = 0$

Sol.

8. Which one of the following aqueous solutions will exhibit highest boiling point ? [AIEEE-2004]

- (A) 0.01 M Na_2SO_4 (B) 0.01 M KNO_3
(C) 0.015 M urea (D) 0.015 M glucose

Sol.

9. Osmotic pressure of 40% (wt./vol.) urea solution is 1.64 atm and that of 3.42% (wt./vol.) cane sugar is 2.46 atm. When equal volumes of the above two solutions are mixed, the osmotic pressure of the resulting solution is -

- (A) 1.64 atm (B) 2.46 atm
(C) 4.10 atm (D) 2.05 atm

Sol.

10. Which of the following liquid pairs shows a positive deviation from Raoult's law ? [AIEEE-2004]

- (A) Water - hydrochloric acid
(B) Benzene - methanol
(C) Water - nitric acid
(D) Acetone - chloroform

Sol.

11. Which one of the following statement is false?

[AIEEE-2004]

(A) Raoult's law states that the vapour pressure of a component over a solution is proportional to its mole fraction

(B) The osmotic pressure (π) of a solution is given by the equation $\pi = MRT$ where M is the molarity of the solution

(C) The correct order of osmotic pressure for 0.01 M aqueous solution of each compound is $\text{BaCl}_2 > \text{KCl} > \text{CH}_3\text{COOH} > \text{sucrose}$.

(D) Two sucrose solutions of same molality prepared in different solvents will have the same freezing point depression.

Sol.

12. If α is the degree of dissociation of Na_2SO_4 , the vant Hoff's factor (i) used for calculating the molecular mass is - [AIEEE-2005]

- (A) $1 - \alpha$ (B) $1 + \alpha$
(C) $1 - 2\alpha$ (D) $1 + 2\alpha$

Sol.

13. Benzene and toluene form nearly ideal solutions. At 20°C, the vapour pressure of benzene is 75 torr and that of toluene is 22 torr. The partial pressure of benzene at 20°C for a solution containing 78 g of benzene and 46 g of toluene in torr is [AIEEE-2005]

- (A) 25 (B) 50
(C) 53.5 (D) 37.5

Sol.

14. Two solutions of a substance (non electrolyte) are mixed in the following manner. 480 ml of 1.5 M first solution + 520 mL of 1.2 M second solution. What is the molarity of the final mixture ? **[AIEEE-2005]**

- (A) 1.50 M (B) 1.20 M
(C) 2.70 M (D) 1.344 M

Sol.

15. Which aqueous solution exhibits highest boiling point – **[AIEEE-2004]**

- (A) 0.015 M glucose (B) 0.01 M KNO_3
(C) 0.015 M urea (D) 0.01M Na_2SO_4

Sol.

16. 18 g of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) is added to 178.2 g of water. The vapour pressure of water for this aqueous solution at 100°C is – **[AIEEE 2006]**

- (A) 7.60 Torr (B) 76.00 Torr
(C) 752.40 Torr (D) 759.00 Torr

Sol.

17. Density of a 2.05 M solution of acetic acid in water is 1.02 g/mL. The molality of the solution is – **[AIEEE 2006]**

- (A) 3.28 mol kg^{-1} (B) 2.28 mol kg^{-1}
(C) 0.44 mol kg^{-1} (D) 1.14 mol kg^{-1}

Sol.

18. A mixture of ethyl alcohol and propyl alcohol has a vapour pressure of 290 mm at 300 K. The vapour pressure of propyl alcohol is 200 mm. If the mole fraction of ethyl alcohol is 0.6, its vapour pressure (in mm) at the same temperature will be – **[AIEEE 2007]**

- (A) 350 (B) 300
(C) 700 (D) 360

Sol.

19. A 5.25% solution of a substance is isotonic with a 1.5% solution of urea (molar mass = 60 g mol^{-1}) in the same solvent. If the densities of both the solutions are assumed to be equal to 1.0 g cm^{-3} , molar mass of the substance will be – **[AIEEE 2007]**

- (A) 90.0 g mol^{-1} (B) 115.0 g mol^{-1}
(C) 105.0 g mol^{-1} (D) 210.0 g mol^{-1}

Sol.

20. The density (in g mL^{-1}) of a 3.60 M sulphuric acid solution that is 29% H_2SO_4 (Molar mass = 98 g mol^{-1}) by mass will be – **[AIEEE 2007]**

- (A) 1.64 (B) 1.88
(C) 1.22 (D) 1.45

Sol.

21. The vapour pressure of water at 20°C is 17.5 mm Hg. If 18g of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) is added to 178.2 g of water at 20°C , the vapour pressure of the resulting solution will be – **[AIEEE 2008]**

- (A) 15.750 mm Hg (B) 16.500 mm Hg
(C) 17.325 mm Hg (D) 17.675 mm Hg

Sol.

22. At 80°C , the vapour pressure of pure liquid 'A' is 520 mm Hg and that of pure liquid 'B' is 1000 mm Hg. If a mixture solution of 'A' and 'B' boils at 80°C and 1 atm pressure, the amount of 'A' in the mixture is (1 atm = 760 mm Hg) **[AIEEE 2008]**

- (A) 34 mol percent (B) 48 mol percent
(C) 50 mol percent (D) 52 mol percent

Sol.

23. A binary liquid solution is prepared by mixing n-heptane and ethanol. Which one of the following statements is correct regarding the behaviour of the solution ? **[AIEEE 2009]**

- (A) The solution is non-ideal, showing +ve deviation from Raoult's Law
(B) The solution is non-ideal, showing –ve deviation from Raoult's Law
(C) n-heptane shows +ve deviation while ethanol shows –ve deviation from Raoult's Law
(D) The solution formed is an ideal solution

Sol.

24. Two liquids X and Y form an ideal solution At 300 K, vapour pressure of the solution containing 1 mol of X and 3 mol of Y is 550 mmHg. At the same temperature, if 1 mol of Y is further added to this solution, vapour pressure of the solution increases by 10 mmHg. Vapour pressure (in mmHg) of X and Y in their pure states will be, respectively - **[AIEEE 2009]**

- (A) 300 and 400 (B) 400 and 600
(C) 500 and 600 (D) 200 and 300

Sol.

25. K_f for water is $1.86\text{ K kg mol}^{-1}$. If your automobile radiator holds 1.0 kg of water, how many grams of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) must you add to get the freezing point of the solution lowered to -2.8°C ? **[AIEEE-2012]**

- (A) 93 g (B) 39 g
(C) 27 g (D) 72 g

Sol.

26. The density of a solution prepared by dissolving 120 g of urea (mol. mass = 60 u) in 1000g of water is 1.15 g/mL. The molarity of this solution is : **[AIEEE-2012]**

- (A) 1.78 M (B) 1.02 M
(C) 2.05 M (D) 0.50 M

Sol.

LEVEL – II

JEE ADVANCED

1. The van't Hoff factor for 0.1 M $\text{Ba}(\text{NO}_3)_2$ solution is 2.74. The degree of dissociation is [JEE 1999]
 (A) 91.3% (B) 87% (C) 100% (D) 74%

Sol.

2. In the depression of freezing point experiment, it is found that [JEE 1999]

- (I) The vapour pressure of the solution is less than that of pure solvent.
 (II) The vapour pressure of the solution is more than that of pure solvent.
 (III) Only solute molecules solidify at the freezing point.
 (IV) Only solvent molecules solidify at the freezing point

(A) I, II (B) II, III (C) I, IV (D) I, II, III

Sol.

3. To 500 cm^3 of water, 3×10^{-3} kg of acetic is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point? K_f and density of water are $1.86 \text{ K kg}^{-1} \text{ mol}^{-1}$ and 0.997 g cm^{-3} respectively. [JEE 2000]

Sol.

4. The vapour pressure of two miscible liquids (A) and (B) are 300 and 500 mm of Hg respectively. In a flask 10 mole of (A) is mixed with 12 mole of (B). However, as soon as (B) is added, (A) starts polymerising into a completely insoluble solid. The polymerisation follows first-order kinetics. after 100 minute, 0.525 mole of a solute is dissolved which arrests the polymerisation completely. The final vapour pressure of the solution is 400 mm of Hg. Estimate the rate constant of the polymerisation reaction. Assume negligible volume change on mixing and polymerisation and ideal behaviour for the final solution. [JEE 2001]

Sol.

5. During depression of freezing point in a solution, the following are in equilibrium [JEE 2003]

- (A) Liquid solvent-solid solvent
 (B) Liquid solvent-solid solute
 (C) Liquid solute-solid solute
 (D) Liquid solute-solid solvent

Sol.

6. Match the boiling point with K_b for x, y and z, if molecular weight of x, y and z are same. [JEE 2003]

	b. pt.	K_b
x	100	0.68
y	27	0.53
z	253	0.98

Sol.

7. A 0.004 M solution of Na_2SO_4 is isotonic with a 0.010 M solution of glucose at same temperature. The apparent degree of dissociation of Na_2SO_4 is : [JEE 2004]

- (A) 25% (B) 50% (C) 75% (D) 85%

Sol.

8. 1.22 g of benzoic acid is dissolved in (i) 100 g acetone (K_b for acetone = 1.7) and (ii) 100 g benzene (K_b for benzene = 2.6). The elevation in boiling points T_b is 0.17°C and 0.13°C respectively. [JEE 2004]

(a) What are the molecular weights of benzoic acid in both the solutions?

(b) What do you deduce out of it in terms of structure of benzoic acid?

Sol.

9. The elevation in boiling point, when 13.44 g of freshly prepared CuCl_2 are added to one kilogram of water, is [Some useful data, $K_b(\text{H}_2\text{O}) = 0.52 \text{ kg K mol}^{-1}$, mol. wt. of $\text{CuCl}_2 = 134.4 \text{ gm}$] [JEE 2005]

- (A) 0.05 (B) 0.1
(C) 0.16 (D) 0.21

Sol.

10. 72.5 g of phenol is dissolved in 1 kg of a solvent ($k_f = 14$) which leads to dimerization of phenol and freezing point is lowered by 7 kelvin. What percent of total phenol is present in dimeric form? [JEE 2006]

Sol.

11. When 20 g of naphtholic acid ($\text{C}_{11}\text{H}_8\text{O}_2$) is dissolved in 50 g of benzene ($K_f = 1.72 \text{ K kg mol}^{-1}$), a freezing point depression of 2 K is observed. The van't Hoff factor (i) is : [JEE 2007]

- (A) 0.5 (B) 1 (C) 2 (D) 3

Sol.

Paragraph for Question No. Q.12 to Q.14

Properties such as boiling point, freezing point and vapour pressure of a pure solvent change when solute molecules are added to get homogeneous solution. These are called colligative properties. Applications of colligative properties are very useful in day-to-day life. One of its examples is the use of ethylene glycol and water mixture as anti-freezing liquid in the radiator of automobiles.

A solution **M** is prepared by mixing ethanol and water. The mole fraction of ethanol in the mixture is 0.9.

Given : Freezing point depression constant of water

$$(K_f^{\text{Water}}) = 1.86 \text{ K kg mol}^{-1}$$

Freezing point depression constant of ethanol

$$(K_f^{\text{Ethanol}}) = 2.0 \text{ K kg mol}^{-1}$$

Boiling point elevation constant of water

$$(K_b^{\text{Water}}) = 0.52 \text{ K kg mol}^{-1}$$

Boiling point elevation constant of ethanol

$$(K_b^{\text{Ethanol}}) = 1.2 \text{ K kg mol}^{-1}$$

Standard freezing point of water = 273 K

Standard freezing point of ethanol = 155.7 K

Standard boiling point of water = 373 K

Standard boiling point of ethanol = 351.5 K

Vapour pressure of pure water = 32.8 mm Hg

Vapour pressure of pure ethanol = 40 mm Hg

Molecular weight of water = 18 g mol^{-1}

Molecular weight of ethanol = 46 g mol^{-1}

In answering the following questions, consider the solutions to be ideal dilute solutions and solutes to be non-volatile and non-dissociative. [JEE 2008]

12. The freezing point of the solution **M** is

- (A) 268.7 K (B) 268.5 K
(C) 234.2 K (D) 150.9 K

Sol.

13. The vapour pressure of the solution **M** is

- (A) 39.3 mm Hg (B) 36.0 mm Hg
(C) 29.5 mm Hg (D) 28.8 mm Hg

Sol.

14. Water is added to the solution **M** such that the mole fraction of water in the solution becomes 0.9. The boiling point of this solution is:

- (A) 380.4 K (B) 376.2 K
(C) 375.5 K (D) 354.7 K

Sol.

15. The Henry's law constant for the solubility of N_2 gas in water at 298 K is 1.0×10^5 atm. The mole fraction of N_2 in air is 0.8. The number of moles of N_2 from air dissolved in 10 moles of water at 298 K and 5 atm pressure is :

[JEE 2009]

- (A) 4.0×10^{-4} (B) 4.0×10^{-5}
(C) 5.0×10^{-4} (D) 5.0×10^{-5}

Sol.

16. The freezing point (in $^{\circ}\text{C}$) of a solution containing 0.1 g of $K_3[Fe(CN)_6]$ (Mol. Wt. 329) in 100 g of water ($K_f = 1.86 \text{ K kg mol}^{-1}$) is

[JEE 2011]

- (A) -2.3×10^{-2} (B) -5.7×10^{-2}
(C) -5.7×10^{-3} (D) -1.2×10^{-2}

Sol.

17. For a dilute solution containing 2.5 g of a non-volatile non-electrolyte solute in 100 g of water, the elevation in boiling point at 1 atm pressure is 2°C . Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure (mm of Hg) of the solution is (take $K_b = 0.76 \text{ K kg mol}^{-1}$)

[JEE 2012]

- (A) 724 (B) 740 (C) 736 (D) 718

Sol.

18. Benzene and naphthalene form an ideal solution at room temperature. For this process the true statement(s) is (are)

[JEE 2013]

- (A) ΔG is positive (B) ΔS_{system} is positive
(C) $\Delta S_{\text{surrounding}} = 0$ (D) $\Delta H = 0$

Sol.

ANSWER-KEY**Answer Ex-I****OBJECTIVE PROBLEMS (JEE MAIN)**

1. B 2. D 3. C 4. A 5. B 6. B 7. D 8. A 9. C 10. D
 11. A 12. D 13. C 14. B 15. C 16. D 17. C 18. D 19. C 20. D
 21. C 22. B 23. B 24. C 25. C 26. C 27. B 28. D 29. B 30. B
 31. C 32. B 33. C 34. A 35. C 36. D 37. B 38. D 39. C 40. D
 41. D 42. C 43. D 44. D 45. A 46. C 47. B 48. B 49. B 50. A

Answer Ex-II**OBJECTIVE PROBLEMS (JEE ADVANCED)**

1. BCD 2. AB 3. AC 4. ACD 5. B 6. A 7. B 8. A
 9. A 10. D 11. A 12. C 13. A 14. D 15. A 16. B
 17. A 18. D 19. C 20. A-Q, B-P, C-R 21. A-R, B-T, C-S, D-P, E-Q
 22. A 23. A 24. B 25. D 26. B 27. B 28. A
 29. A 30. ACD

Answer Ex-III**SUBJECTIVE PROBLEMS (JEE ADVANCED)**

1. 0.24 2. 0.25 3. 24.5 torr 4. 57.24 g/mol 5. 66.13 mm Hg 6. 0.237 7. 0.682, 0.318; 0.829, 0.171
 8. 92 mol% toluene; 96.8 mol% toluene 9. $P_A^0 = 213.33$ torr, $P_B^0 = 960.0$ torr 10. 0.04 11. 111.1 g, 18.52 molal
 12. 0.741 m, 0.013 13. 0.162 m 14. 65.25 15. 17.38 16. 0.964 17. 106 g/mol 18. 64.0 g/mol
 19. 100.079°C 20. -0.62°C 21. 5.08°C/m 22. 50.8 g/mol 23. 2050 g/mol 24. $x=25.6$ $y=42.6$
 25. $K_b = 0.512$ Kg mol K^{-1} , $T_b = 373.20$ K 26. 38.71 g 27. 156.06 28. C_6H_6 29. $T_f = -2.28^\circ C$
 30. $P = 0.2217$ atm should be applied 31. ($V_{final} = 5 \cdot V_{original}$) 32. 54.2 g 33. 0.81 atm 34. 13.8 atm

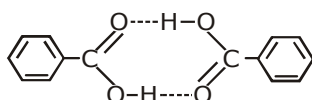
35. 5.4×10^5 g/mol 36. 2.4×10^5 gm/mole 37. 59.99 38. $M_A/M_B=0.33$ 39. $i = 2.5$ 40. 3 ions
41. $\alpha = 99.2\%$ 42. $7.482 \times 10^5 \text{ Nm}^{-2}$ 43. 94.5% 44. 4.64 atm 45. 0.95, 1.95
46. $\text{C}_{44}\text{H}_{88}\text{O}_{44}$ 47. (a) 3.79°C , (b) 0.018, (c) 4.65 atm, (d) 251.5 48. 0.93 49. $x_b = 0.2472$, $Y_b = 0.4473$
50. 46.33°C 51. 0.73 52. $M = 53.8$
53. (a) 0.47, (b) 565 torr, (c) $x_A=0.08$, $x_B = 0.92$, (d) 675 torr, (e) $x'_A=0.11$, $x'_B=0.89$ 54. 746.24 mm/Hg
55. (a) 210.65, (b) 62.35% 56. 18.34% 57. $T_b = 102.3^\circ\text{C}$ 58. $T_f = -0.73^\circ\text{C}$ 59. $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
60. $x_a=0.1$ 61. $a = 0.7333$ 62. -19.91°C , 7.63 M 63. 20.11% 64. 5.4×10^{-13} 65. 8.9 gm
66. 12.54 67. 12.72 68. $K = 3.36$ 69. (i) $K_a = 7.3 \times 10^{-3}$ (ii) 4.55×10^{22}

Answer Ex-IV**PREVIOUS YEARS PROBLEMS****LEVEL – I****JEE MAIN**

1. A 2. B 3. A 4. D 5. C 6. C 7. B
8. A 9. D 10. B 11. D 12. D 13. B 14. D
15. D 16. C 17. B 18. A 19. D 20. C 21. C
22. C 23. A 24. B 25. A 26. C

LEVEL – II**JEE ADVANCED**

1. B 2. C 3. 0.229 4. 1.0×10^{-4} 5. A 6. $K_b(x) = 0.68$, $K_b(y) = 0.53$, $K_b(z) = 0.98$
7. C 8. (a) 122, (b) It means that benzoic acid remains as it is in acetone while it dimerises in benzene as



9. C 10. 35% phenol is present in dimeric form 11. A 12. D 13. B 14. B 15. A
16. A 17. A 18. BCD

IONIC EQUILIBRIUM

1. ELECTRIC CONDUCTIVITY

Those substance which allow the electric current to pass through them are called electric conductors and property is called electric conductivity.

On the basis of Electric conductivity, substances are of two types -

1.1 Non-conductors :

Those substance which do not allow the electric current to pass through them are called nonconductors. eg. All covalent compounds & nonmetals.

1.2 Conductors :

Those substance which allow the electric current to pass through them are called conductors. eg. all metals, alloys, all acid and bases, salt and graphite etc.

On the basis of conducting units conductors are of two types -

1.2.1 Metallic or Electric Conductors :

Electricity conduct them due to the presence of free and mobile electron which act as electricity conducting unit called metallic or electric conductors. eg. Metals, Alloys, Graphite, Gas, Carbon etc.

1.2.2 Ionic Conductors or Electrolytes :

Conductors in which the current is passes through them due to the presence of free ions are called **Ionic Conductors or Electrolyte or Electrolytic conductors**.

Ionic conductors are further divided into two types on the basis of their strengths -

(a) Strong electrolytes :

(i) Those substance which are almost completely ionize into ions in their aqueous solution are called strong electrolytes.

(ii) Degree of ionisation for this type of electrolyte is one i.e. $\alpha \cong 1$. eg. HCl, H_2SO_4 , NaCl, HNO_3 , KOH, NaOH, HNO_3 , $AgNO_3$, $CuSO_4$, etc. Means all strong acids and bases and all types of salts.

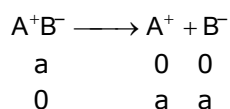
(b) Weak electrolytes :

(i) Those substance which are ionize to a small extent in their aqueous solution are known weak electrolytes. eg. H_2O , CH_3COOH , NH_4OH , HCN, $HCOOH$, Liq. SO_2 etc. Means all weak acids and bases.

(ii) Degree of ionization for this types of electrolytes in $\alpha \ll 1$.

Concept of electrolyte

Strong electrolyte

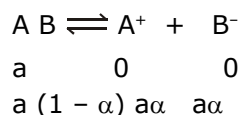


100% dissociaation ($\alpha = 1$)

no equilibrium

it is irreversible

Weak electrolyte



$\alpha < 1$

equilibrium

it is reversible process.

ARRHENIUS THEORY OF ELECTROLYTIC DISSOCIATION OR IONIZATION

- (a) When an electrolyte dissociates into water, it gives two types of charged particles called ions.
- (b) Ions which carry (+) ve charge and move towards cathode are called as '**Cations**' while ions carrying (-) ve charge and moving towards anode called as '**anion**'.
- (c) Every electrolytic solution is always neutral in nature.
- (d) Quantity or part of electrolyte which is ionized or decomposed or dissociate called as "**Degree of Ionisation**".
- (e) Electrolyte which gives H^+ ions after dissociation in the aqueous solution is called as acid while that which gives OH^- after dissociation in the aqueous solution is called as base.
- (f) Acidic strength of acids is directly proportional to the dissociation constant K_a .
- $pK_a = -\log K_a$

$$\text{Thus, Acidic strength} \propto K_a \propto \frac{1}{pK_a} \propto pK_b \propto \frac{1}{K_b}$$

- (g) Similarly basic strength of bases is directly proportional to K_b .

$$pK_b = -\log K_b$$

$$\text{Basic strength of base} \propto K_b \propto \frac{1}{pK_b} \propto pK_a \propto \frac{1}{K_a}$$

- (h) Conductivity of solution depends upon the number of ions produced by the electrolyte, such as -
Conduction of solution \propto number of ions produced by the electrolyte

- (i) Solution of strong electrolyte has more electric conductivity property as compared to weak electrolyte.
- (j) Only weak electrolyte followed the law of mass action and **Ostwalds dilution law**.
- (k) When electricity passed through in the electrolytic solution, it gives only direction to movement of ions towards the electrodes.
- (l) Movement of ions is inversely proportional to the molecular mass or atomic mass of ions.

Limitations of Arrhenius Concept : -

- (a) H^+ and OH^- ions exist as hydrated ions.
- (b) He was unable to explain the acidic nature of CO_2 , SO_2 etc. and basic nature of NH_3 , CaO , Na_2CO_3 etc.
- (c) He could not explain the acid base reaction in the absence of water.
- $$SO_3(g) + CaO(s) \rightarrow CaSO_4(g)$$

Factors affecting the degree of ionisation : -

- (a) **Temperature** - With the rise in temperature, the degree of dissociation of an electrolyte in solution increased. Thus,
Degree of dissociation \propto Temperature
- (b) **Dilution** : - On the increasing of dilution, the degree of dissociation increases. But at infinite dilution, there is no effect on the degree of dissociation.
- (c) **Concentration of the solution** : -

$$\text{Degree of dissociation} \propto \frac{1}{\text{Concentration of solution}} \propto \frac{1}{\text{Amount of solute in given volume or wt. of solution}} \propto \text{Amount of solvent}$$

(d) **Nature of Solvent** :- Higher the dielectric constant of a solvent, more is its dissociation power or ionising power. Thus

Degree of ionisation or dissociation of an electrolyte \propto dielectric constant of solvent.

Dielectric constant :- The dielectric constant of solvent is a measure of its tendency to weaken the forces of attraction between oppositely charged ions of the given electrolyte or the force of attraction applied by solvent molecules on solute molecule is defined as Dielectric constant of solvent.

Note :- Water is the most powerful ionizing solvent as its dielectric constant is highest.

(e) **Presence of Common Ion** :- In the presence of a strong electrolyte having common ion, the degree of dissociation of an electrolyte decreases. eg. Ionisation of CH_3COOH is suppressed in the presence of HCl due to common H^+ ions.

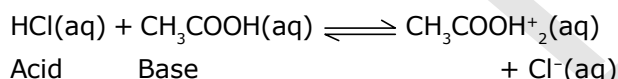
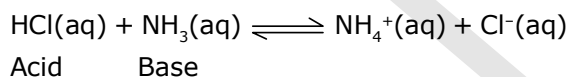
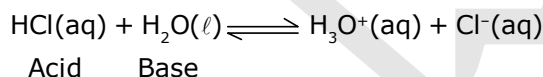
(f) **Nature of Electrolyte** :- At constant temperature, electrolytes ionize to a different extent in their solutions of same concentration.

BRONSTED AND LOWRY CONCEPT OF ACIDS & BASES

Postulates :-

- (1) Acid - Proton (H^+) donor
- (2) Base - Proton (H^+) acceptor

e.g.



Note :- Here CH_3COOH has a less tendency to donate H^+ than HCl , therefore CH_3COOH acts as a weak base.

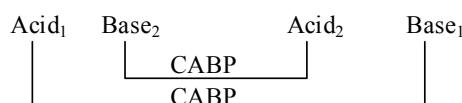
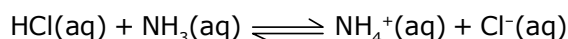
Conjugate Acid-Base Pair (CABP) :-

In an acid-base reaction

Acid $\longrightarrow \text{H}^+$ + conjugate base

Base + H^+ \longrightarrow conjugate acid.

e.g.



Note:- A CABP is different from each other only by single proton.

e.g.

HSO_4^- is the conjugate base of H_2SO_4 but SO_4^{2-} is not.

Relative strength of Acids/Bases :-

Any Species and its conjugate species are opposite of each other in terms of strength. e.g.

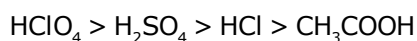
Acid (or Base) Conjugate Base (or Acid)

(i) Weak Strong

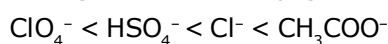
(ii) Strong Weak

e.g.

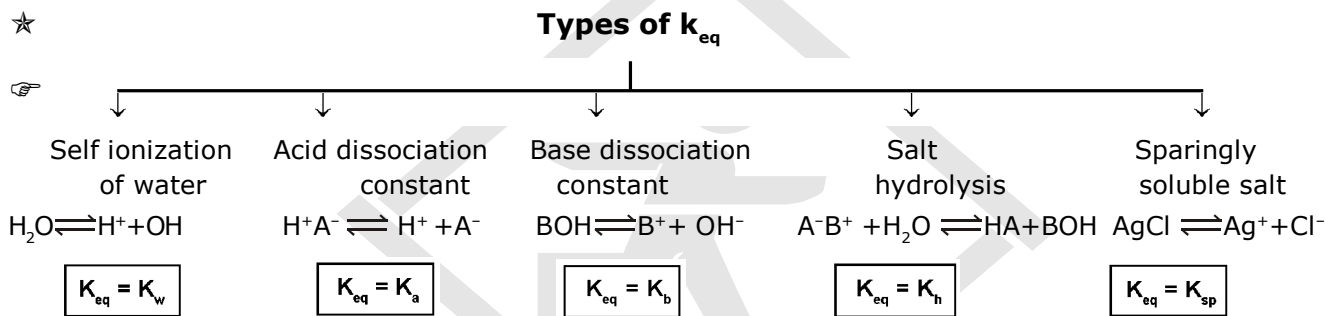
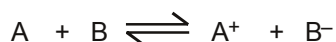
Strength order of acids.



strength order of conjugate bases



An ionic Equilibrium exists between the unionised electrolyte molecules and the ions that result from ionisation



★

Self ionization of water

$$\text{Concentration of } \text{H}_2\text{O} ([\text{H}_2\text{O}]) = \frac{1000 / 18}{1} = 55.5 \text{ M}$$

Water is very weak electrolyte



55.5

$55.5 \times 10^{-7} \quad 10^{-7} \quad 10^{-7}$ (at 25°C)

☞

$$k_{\text{eq}} = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

Constant

☞

$$K_w = k_{\text{eq}} [\text{H}_2\text{O}] = [\text{H}^+][\text{OH}^-]$$

$K_w = [H^+][OH^-]$, at $25^\circ C$, $[H^+] = [OH^-] = 10^{-7}$
 $K_w(25^\circ C) = 10^{-14}$

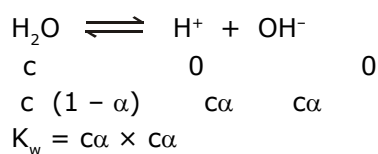
↓

Self ionization constant of water

let, K_{w_1} at temperature T_1 , K_{w_2} at temperature T_2

$\log \frac{K_{w_2}}{K_{w_1}} = \frac{\Delta H}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$, $T \uparrow \Rightarrow K_w \uparrow$

For calculation of α :



$\alpha = \frac{\sqrt{K_w}}{c}$ $c = 5.56 \text{ M}$ $\alpha = 1.8 \times 10^{-2} \sqrt{K_w}$

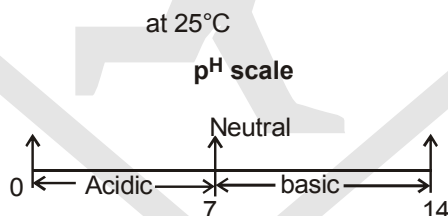
pH

(pH scale is given by Sorenson)

potent
 ↓
 strength

Hydrogen ion

$pH = -\log [H^+]$
 $pOH = -\log [OH^-]$
 $pK_w = -\log K_w$
 at any temperature :
 $[H^+] = [OH^-]$
 $[H^+][OH^-] = K_w$



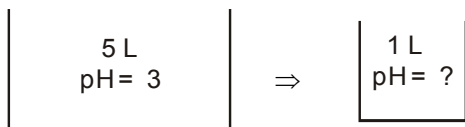
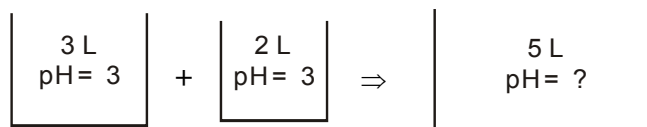
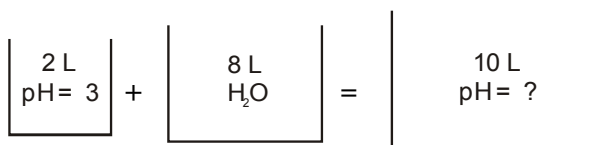
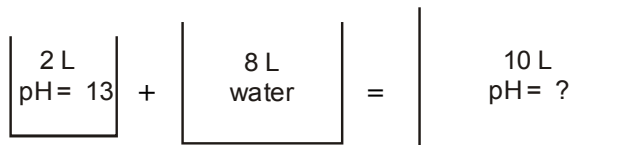
$-\log [H^+] - \log [OH^-] = -\log [K_w]$

$pH + pOH = pK_w$

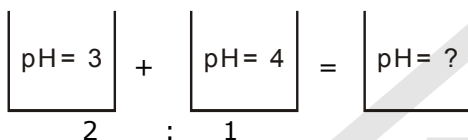
at $25^\circ C$
 $K_w = 10^{-14}$
 $pH + pOH = 14$

at $80^\circ C$
 $K_w = 10^{-12}$
 $pH + pOH = 12$

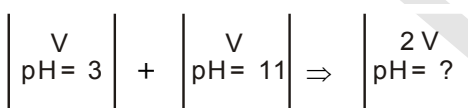
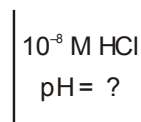
Some concept regarding pH calculation

☞ **Concept 1 :**☞ **Concept 2:**☞ **Concept 3:**☞ **Concept 4:**

☞ **Note :** $\xleftarrow{\text{Calculate pH}} 7 \xrightarrow{\begin{array}{l} \text{(i) Calculate pOH} \\ \text{(ii) pH} = 14 - \text{pOH} \end{array}}$

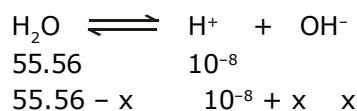
☞ **Concept 5:**

☞ **Note :** The final pH of solution after mixing two solution is in between the previous solution pH.

☞ **Concept 6:**☞ **Concept 7:**☞ **Note :**

When $[\text{H}^+] > 10^{-5} \Rightarrow [\text{H}^+]_{\text{water}}$ neglected

When $[\text{H}^+] < 10^{-5} \Rightarrow [\text{H}^+]_{\text{water}}$ considered



☞ $x(10^{-8} + x) = 10^{-14} \Rightarrow x = .94 \times 10^{-7}$

☞ $[\text{H}^+] = 10^{-8} + .94 \times 10^{-7} = 1.04 \times 10^{-7}$

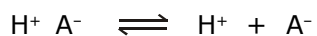
☞ $\text{pH} = 7 - \log(1.04)$

Concept 8:

$$10^2 \text{ M HCl}$$

$$\text{pH} = ?$$

$$\text{pH} = -\log [\text{Active mass}]$$

Dissociation of weak acid :


c

$$c(1-\alpha) \quad c\alpha \quad c\alpha$$

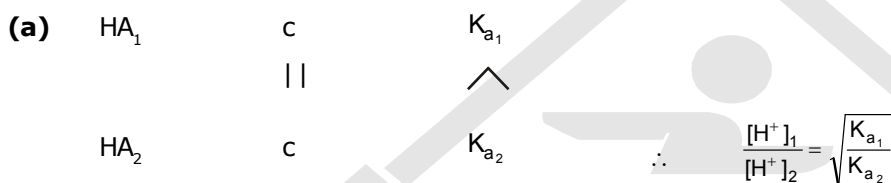
$$K_a = \frac{c\alpha^2}{1-\alpha}$$

for weak acid $\alpha < < 1$

$$K_a = c\alpha^2$$

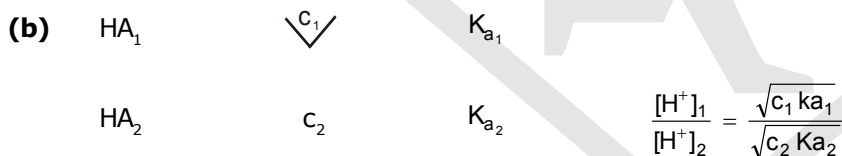
$$\alpha = \sqrt{\frac{K_a}{c}}$$

$$[\text{H}^+] = c\alpha = \sqrt{cK_a}, \quad \text{pH} = -\log \sqrt{cK_a}, \quad \text{for weak bases } [\text{H}^+] = \frac{K_w}{\sqrt{c \times K_b}} = \frac{K_w}{[\text{OH}^-]}$$

Note :


So HA_2 is stronger acid than

HA_1



The acidic strength of two weak acid can be compared by K_a value only in the case when their concentration are same. Otherwise the procedure of case (b) should be followed.

pH of mixture of two acids

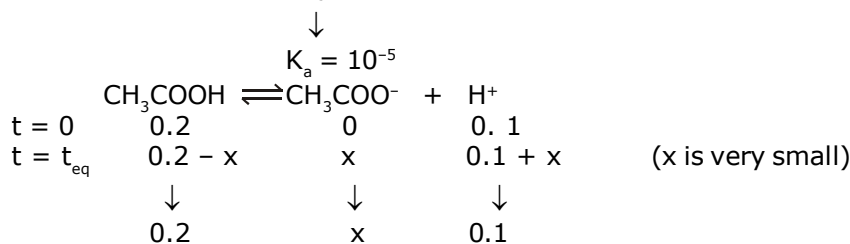
Case I
S.A. + W. A.

Case II
W. A. + W. A.

Case II - A
 K_{as} are incomparable

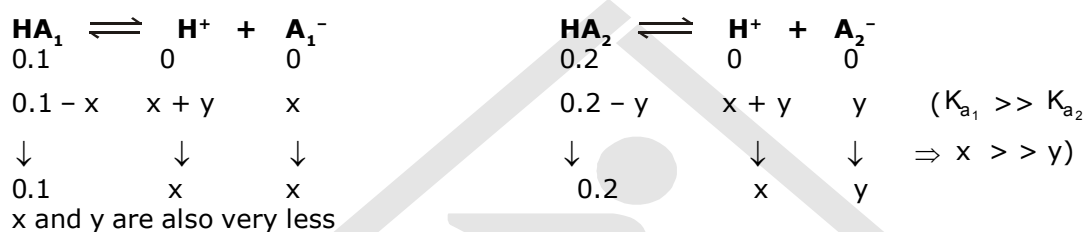
Case II - B
 K_{as} are comparable

★

Case (I) (Strong acid + weak acid)**Question :** HCl (0.1 M) + CH₃COOH (0.2 M)

$$\Rightarrow \text{pH} = -\log(0.1) = 1 \quad \Rightarrow [\text{CH}_3\text{COO}^-] = ? \quad \Rightarrow 10^{-5} = \frac{x \times 0.1}{0.2} \Rightarrow [\text{CH}_3\text{COO}^-] = 2 \times 10^{-5}$$

★

Case (II-A) (weak acid + weak acid) (k_{as} are incomparable)**Question :** HA₁ (0.1 M, K_{a1} = 10⁻⁵)HA₂ (0.2 M, K_{a2} = 10⁻⁹)

$$10^{-5} = \frac{x \cdot x}{10^{-1}} \quad [\text{H}^+] = x = 10^{-3}, \Rightarrow \text{pH} = 3 \quad [\text{A}_1^-] = \quad [\text{A}_2^-] =$$

★

Case (II-B) (weak acid + weak acid) (k_{as} are comparable)**Question :** HA₁ (0.1)K_{a1} = 10⁻⁵HA₂ (0.2)K_{a2} = 10⁻⁶

$$\Rightarrow \text{now } K_{a1} = \frac{x(x+y)}{0.1}$$

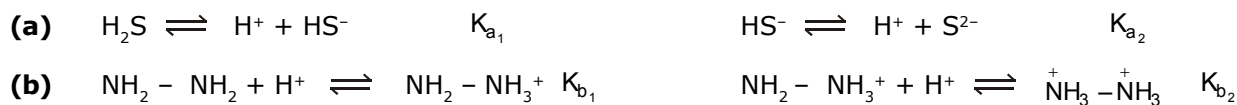
$$\Rightarrow K_{a1} = \frac{x(x+y)}{c_1}, \quad K_{a2} = \frac{(x+y)y}{c_2}$$

$$\Rightarrow x(x+y) = c_1 K_{a1} \quad y(x+y) = c_2 K_{a2}$$

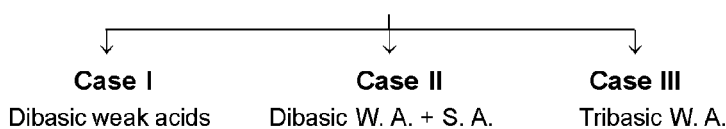
$$(x+y)^2 = c_1 K_{a1} + c_2 K_{a2}$$

$$\Rightarrow [\text{H}^+] = x + y = \sqrt{c_1 K_{a1} + c_2 K_{a2}}$$

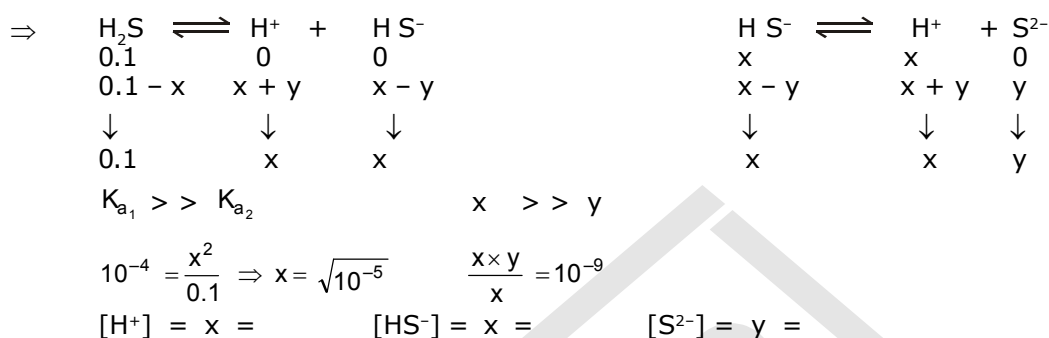
☞ weak polyprotic acids or bases
(H_2S , H_3PO_4 , $\text{NH}_2 - \text{NH}_2$, H_2CO_3)



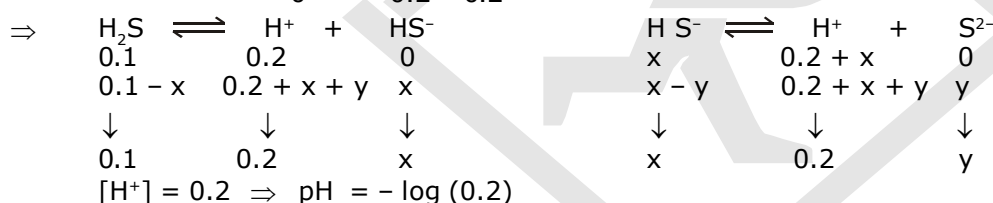
Cases



☞ **Case I :** H_2S (0.1 M) $K_{a_1} = 10^{-4}$, $K_{a_2} = 10^{-9}$



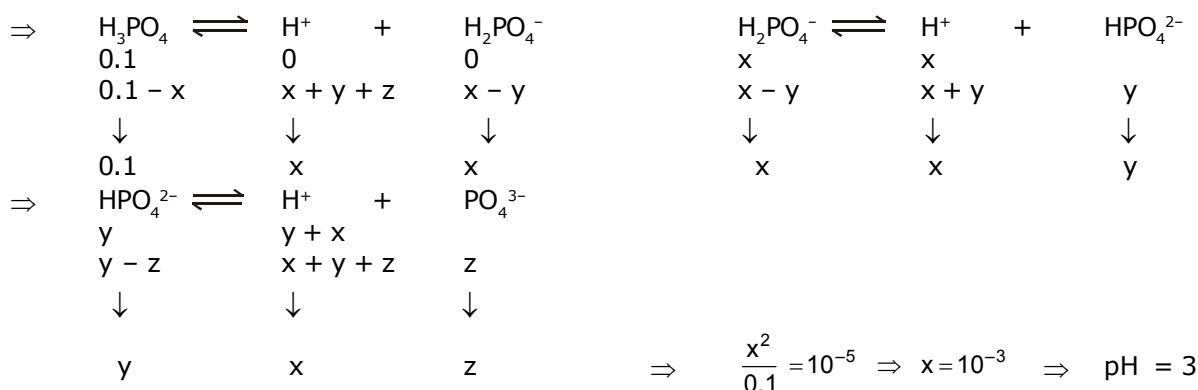
★ **Case II :** $\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$



☞ **Note :** Strong acid controls the pH.

☞ Now, $[\text{H}^+] = 0.2$

★ **Case III :** H_3PO_4 (0.1 M) $K_{a_1} = 10^{-5}$, $K_{a_2} = 10^{-8}$, $K_{a_3} = 10^{-11}$





Buffer



Any solution which resist the change in pH is called Buffer solution.



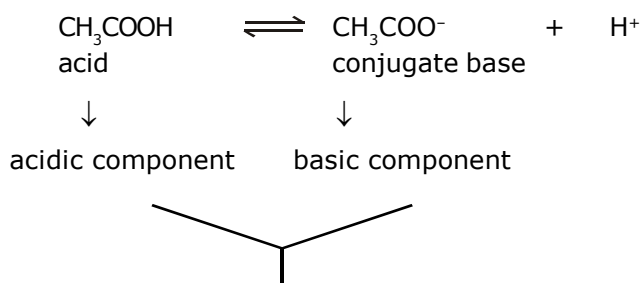
Requirement of Buffer



(1) Must have acidic and basic components so that it can consume H^+ , OH^- added to the buffer.



(2) Acidic and basic components should not react with each other.



do not react with each other.



(3) Buffers can be prepared by following two ways

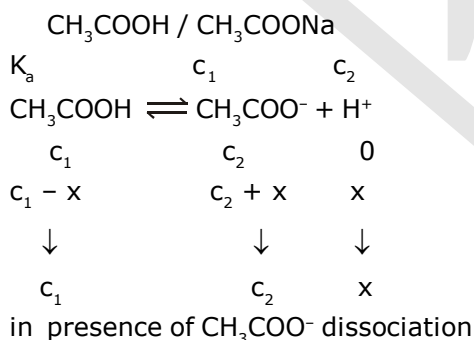


Buffer

CH_3COOH / CH_3COONa
 W. A / Conjugate Base
 \Rightarrow acidic buffer
 $\Rightarrow 0 < pH < 14$

NH_4OH / NH_4Cl
 W. B / Conjugate acid
 \Rightarrow basic buffer
 $\Rightarrow 0 < pH < 14$

Acidic buffer



of CH_3COOH is suppressed.

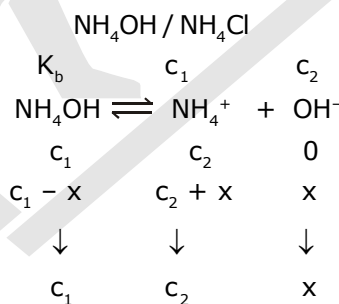
So x is very small

$$K_a = \frac{c_2 \cdot x}{c_1}$$

$$\Rightarrow x = \frac{K_a c_1}{c_2}$$

$$pH = pK_a + \log \frac{c_2}{c_1}$$

Basic buffer



$$K_b = \frac{c_2 \cdot x}{c_1}$$

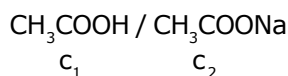
$$x = K_b \frac{c_1}{c_2}$$

$$pOH = pK_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

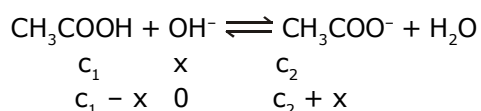
Buffer action

Acidic



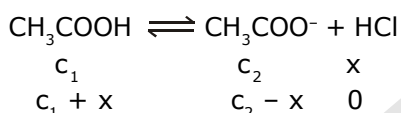
$$\text{pH} = \text{pK}_a + \log \frac{c_2}{c_1}$$

(a) NaOH is added (x M)



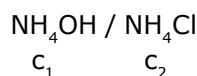
$$\text{pH} = \text{pK}_a + \log \frac{c_2 + x}{c_1 - x}$$

(b) HCl is added (x M)



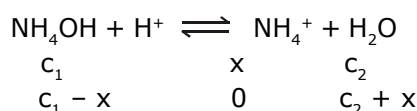
$$\text{pH} = \text{pK}_a + \log \frac{c_2 - x}{c_1 + x}$$

Basic



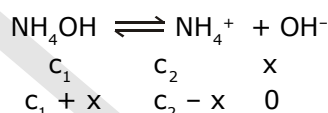
$$\text{pOH} = \text{pK}_b + \log \frac{[c_2]}{[c_1]}$$

(a) HCl is added (x M)



$$\text{pOH} = \text{pK}_b + \log \frac{c_2 + x}{c_1 - x}$$

(b) NaOH is added (x M)



$$\text{pOH} = \text{pK}_b + \log \frac{c_2 - x}{c_1 + x}$$

How to prepare buffer

Acidic buffer

 (a) $\text{CH}_3\text{COOH} / \text{CH}_3\text{COONa}$

$$\begin{array}{cc} c_1 & c_2 \\ \text{pH} = \text{pK}_a + \log \frac{c_2}{c_1} \end{array}$$

 (b) $\text{CH}_3\text{COOH} + \text{NaOH} \rightleftharpoons \text{CH}_3\text{COONa} + \text{H}_2\text{O}$

$$\begin{array}{ccccc} a & & x & & \\ a - x & & 0 & & x \\ \text{pH} = \text{pK}_a + \log \frac{x}{a - x} \end{array}$$

 (c) $\text{CH}_3\text{COONa} + \text{HCl} \rightleftharpoons \text{CH}_3\text{COOH} + \text{NaCl}$

$$\begin{array}{ccccc} a & & x & & 0 \\ a - x & & 0 & & x \\ \text{pH} = \text{pK}_a + \log \frac{a - x}{x} \end{array}$$

Basic buffer

 (a) $\text{NH}_4\text{OH} / \text{NH}_4\text{Cl}$

$$\begin{array}{cc} c_1 & c_2 \\ \text{pOH} = \text{pK}_b + \log \frac{c_2}{c_1} \end{array}$$

 (b) $\text{NH}_4\text{OH} + \text{HCl} \rightleftharpoons \text{NH}_4\text{Cl} + \text{H}_2\text{O}$

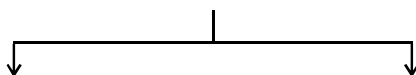
$$\begin{array}{ccccc} a & & x & & 0 \\ a - x & & 0 & & x \\ \text{pOH} = \text{pK}_b + \log \frac{x}{a - x} \end{array}$$

 (b) $\text{NH}_4\text{Cl} + \text{NaOH} \rightleftharpoons \text{NH}_4\text{OH} + \text{NaCl}$

$$\begin{array}{ccccc} a & & x & & \\ a - x & & 0 & & x \\ \text{pOH} = \text{pK}_b + \log \frac{a - x}{x} \end{array}$$



Parameters of buffer



Buffer range

The range of pH a buffer can work nicely is called buffer range

$$\text{pH} = \text{pK}_a + \log \frac{\text{salt}}{\text{acid}}$$

after buffer action

$$\text{pH} = \text{pK}_a + \log \frac{c_2 - x}{c_1 + x}$$

$$\text{min. ratio} \left(\frac{[\text{salt}]}{[\text{acid}]} \right) = 0.1$$

$$\text{pH} = \text{pK}_a - 1$$

$$\text{pK}_a - 1 \quad \text{pK}_a \quad \text{pK}_a + 1$$

Requirement of good buffer

(1) $\text{pH} = \text{pK}_a$
resist both OH^- and H^+ in equal amount

$$(2) \quad \text{pH} = \text{pK}_a + \log \frac{c_2}{c_1}$$

$$\text{max. ratio} \left(\frac{[\text{salt}]}{[\text{acid}]} \right) = 10$$

$$\Rightarrow \text{pH} = \text{pK}_a + 1$$

both will be approximately same when

c_1 and c_2 are very large

$$c_1, c_2 \gg x$$

$$\Rightarrow \text{pH} = \text{pK}_a + \log \frac{c_2}{c_1}$$



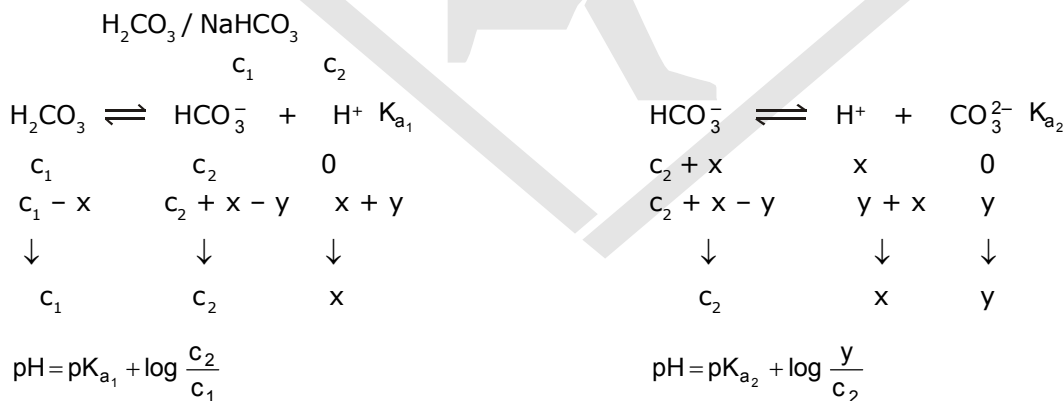
Buffer capacity



$$\text{Buffer Capacity} = \frac{\text{number of mol of H}^+ \text{ added/L of solution}}{\text{Change in pH of buffer}}$$



Buffer of polyprotic acid



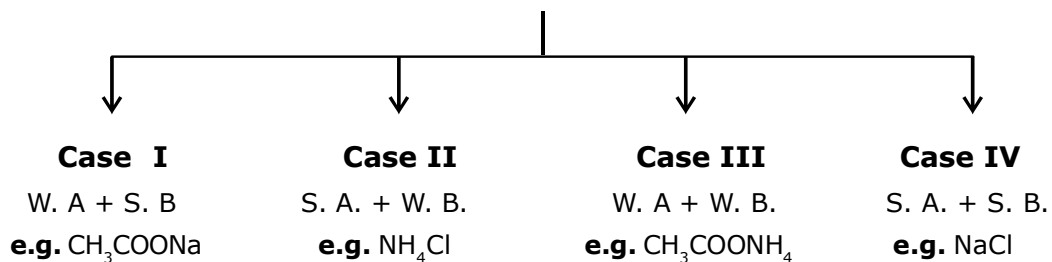
Salt Hydrolysis



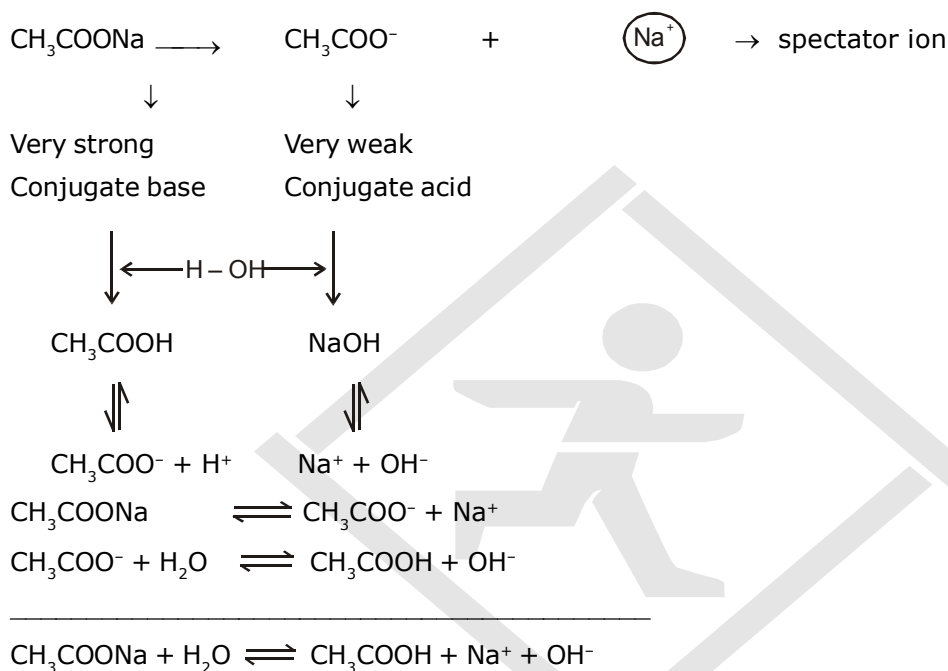
since salt hydrolysis is an endothermic reaction hence on increasing the temperature, the extent of hydrolysis increases.



Types of salt

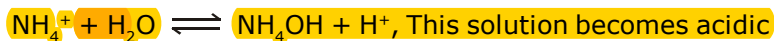


☞ Case : (I) Hydrolysis of WA + SB :

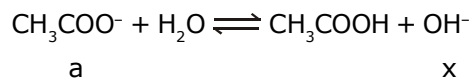


Note : (1) Only weaker part of salt undergoes hydrolysis. **(2)** This solution becomes basic.

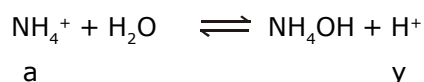
☞ Case : (II) S.A. + W.B. (NH_4Cl) :



☞ Case : (III) W.A. + W.B. ($\text{CH}_3\text{COONH}_4$) :

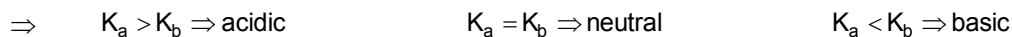


$$a - x$$



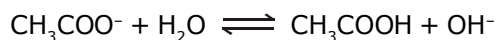
$$a - y$$

Can be acidic, basic or neutral



☞ **Case : (IV) S. A + S. B (NaCl) :**

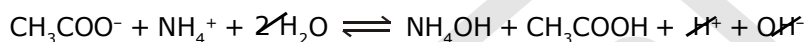
⇒ No hydrolysis ⇒ Solution will be neutral

★ **Relationship between K_a , K_b , and K_h** ☞ **Case (I) : W. A. + S.B. (CH_3COONa)**

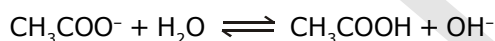
$$\Rightarrow K_{\text{eq}} = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{H}_2\text{O}][\text{CH}_3\text{COO}^-]} \Rightarrow K_h = K_{\text{eq}} [\text{H}_2\text{O}] = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-] \times [\text{H}^+]}{[\text{CH}_3\text{COO}^-] \times [\text{H}^+]} \Rightarrow K_h = \frac{K_w}{K_a}$$

☞ **Case (II) : S. A. + W. B. (NH_4OH)**

$$\Rightarrow K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} \Rightarrow K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+] \times [\text{OH}^-]}{[\text{NH}_4^+] \times [\text{OH}^-]} \Rightarrow K_h = \frac{K_w}{K_b}$$

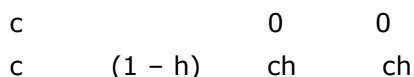
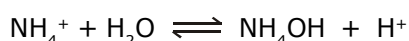
☞ **Case (III) W. A. + W. B. ($\text{CH}_3\text{COO NH}_4$)**

$$\Rightarrow K_h = \frac{[\text{NH}_4\text{OH}][\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-][\text{NH}_4^+]} \Rightarrow K_h = \frac{[\text{NH}_4\text{OH}]}{[\text{NH}_4^+][\text{OH}^-]} \cdot \frac{[\text{CH}_3\text{COOH}][\text{OH}^-][\text{H}^+]}{[\text{CH}_3\text{COO}^-][\text{H}^+]} \Rightarrow K_h = \frac{K_w}{K_a \cdot K_b}$$

★ **pH calculation**☞ **Case (I) : W. A. + S. B. ($\text{CH}_3\text{COONa} \Rightarrow c, K_a$) , $h \rightarrow$ degree of hydrolysis.**

$$\Rightarrow K_h = \frac{(ch)^2}{c(1-h)} = \frac{ch^2}{1-h} \quad h \ll 1 \Rightarrow K_h = ch^2 \Rightarrow h = \sqrt{\frac{K_h}{c}}$$

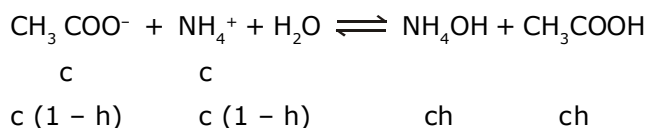
$$\Rightarrow [\text{OH}^-] = c \times h = \sqrt{c \cdot K_h} = \sqrt{c \cdot \frac{K_w}{K_a}} \Rightarrow \text{pOH} = \frac{1}{2} [\text{pK}_w - \text{pK}_a - \log c] \Rightarrow \text{pH} = \frac{1}{2} [\text{pK}_w + \text{pK}_a + \log c]$$

☞ **Case (II) : S. A. + W. B. ($\text{NH}_4\text{Cl} \Rightarrow c, K_b$)**

$$\Rightarrow K_h = \frac{ch^2}{1-h} \quad h \ll 1 \Rightarrow K_h = ch^2 \Rightarrow h = \sqrt{\frac{K_h}{c}}$$

$$\Rightarrow [H^+] = c \cdot h = \sqrt{c \times K_h} = \sqrt{c \times \frac{K_w}{K_b}} \Rightarrow pH = \frac{1}{2} [pK_w - pK_b - \log c] \Rightarrow p^{OH} = \frac{1}{2} [pK_w + pK_b + \log c]$$

☞ **Case (III)** W. A. + W. B. ($CH_3COONH_4 \rightarrow K_a, K_b, c$)



$$\Rightarrow K_h = \frac{c^2 h^2}{c^2 (1-h)^2} = \frac{h^2}{(1-h)^2} \Rightarrow K_h = h^2 \quad 1-h \approx 1 \Rightarrow h = \sqrt{K_h}$$

$$\Rightarrow h = \sqrt{\frac{K_w}{K_a K_b}} \quad \text{----- (1)}$$

$$\Rightarrow CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \Rightarrow K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \Rightarrow [H^+] = K_a \frac{[CH_3COOH]}{[CH_3COO^-]}$$

$$\Rightarrow = K_a \times \frac{ch}{c(1-h)} \quad (h \ll 1) \Rightarrow [H^+] = K_a \cdot h \Rightarrow [H^+] = K_a \cdot \sqrt{\frac{K_w}{K_a K_b}} \quad (\text{from 1})$$

$$\Rightarrow [H^+] = \sqrt{K_w \cdot \frac{K_a}{K_b}} \Rightarrow pH = \frac{1}{2} [pK_w + pK_a - pK_b]$$

☞ **If**, $K_a > K_b \Rightarrow pK_a < pK_b \Rightarrow$ acidic, $K_a = K_b \Rightarrow$ neutral, $K_a < K_b \Rightarrow$ basic

★

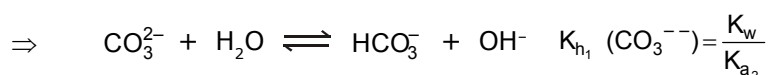
Summary of hydrolysis

1. **W. A. + S. B.** $K_h = \frac{K_w}{K_a} \quad pH = \frac{1}{2} [pK_w + pK_a + \log c]$

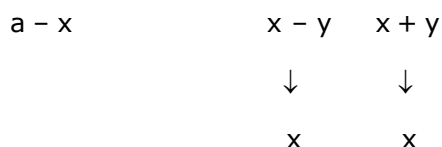
2. **W. B. + S. A.** $K_h = \frac{K_w}{K_b} \quad pH = \frac{1}{2} [pK_w - pK_b - \log c]$

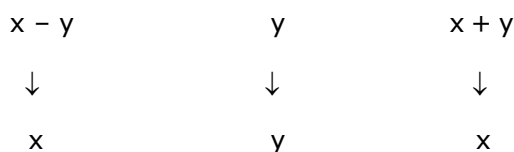
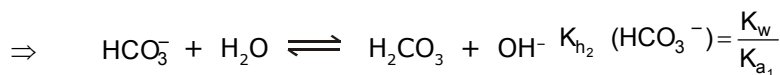
3. **W. A. + W. B.** $K_h = \frac{K_w}{K_a \cdot K_b} \quad pH = \frac{1}{2} [pK_w + pK_a - pK_b]$

★ **Hydrolysis of salt of polyprotic acid / base (Na_2CO_3)**



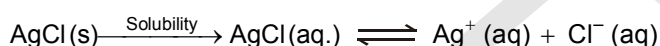
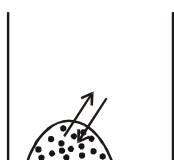
a





$$\Rightarrow [\text{OH}^-] = \sqrt{c \times K_{h_1}} = \sqrt{c \times \frac{K_w}{K_{a_2}}}, \Rightarrow [\text{HCO}_3^-] = [\text{OH}^-] = \sqrt{c \times \frac{K_w}{K_{a_1}}}, \Rightarrow \frac{K_w}{K_{a_1}} = \frac{x \times y}{x} \Rightarrow [\text{H}_2\text{CO}_3] = \frac{K_w}{K_{a_1}}$$

★

Solubility of sparingly soluble salt

⇒ In ionic equilibrium all the components of equilibrium should be in same phase.

⇒ In case of solubility equilibrium of sparingly soluble salt equilibrium is a heterogeneous equilibrium.

☞ **Example (1):** Solubility of AgCl



$$K_{\text{eq}} = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]}$$

$$\Rightarrow K_{\text{sp}} = K_{\text{eq}} \cdot [\text{AgCl}] = [\text{Ag}^+][\text{Cl}^-]$$

⇒ It is an endothermic reaction on increasing temperature $T \uparrow \Rightarrow \text{solubility} \uparrow$

$$\Rightarrow \log \frac{K_{\text{sp}_2}}{K_{\text{sp}_1}} = \frac{\Delta H}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

☞ **Example (2):** Solubility of Ag_2CO_3 $\text{Ag}_2\text{CO}_3(\text{s}) \rightleftharpoons 2\text{Ag}^+ + \text{CO}_3^{2-}$

⇒ $K_{\text{sp}} = [\text{Ag}^+]^2 [\text{CO}_3^{2-}]$, ⇒ In general, if salt is M_xN_y type, $\text{M}_x\text{N}_y \rightleftharpoons x\text{M}^{y+} + y\text{N}^{x-}$

$$\Rightarrow K_{\text{sp}} = [\text{M}^{y+}]^x [\text{N}^{x-}]^y$$

let , $Q = [M^{y+}]^x [N^{x-}]^y$ $Q = \text{ionic product}$

If , $Q = K_{sp} \Rightarrow \text{Equilibrium (Saturated solution)}$ $Q > K_{sp} \Rightarrow \text{Ppt (Super saturated)}$

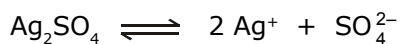
$Q < K_{sp} \Rightarrow \text{Unsaturated solution.}$



Various case in solubility



Case (1): Ag_2SO_4 ($S = 10^{-3} \text{ mol/L}$)



S 0 0

$$0 \quad \quad \quad 2S \quad \quad S \quad \quad K_{sp} = [\text{Ag}^+]^2 [\text{SO}_4^{2-}] = (2S)^2 (S) = 4S^3$$

$$= 4 \times (10^{-3})^3$$



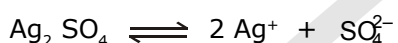
Case (2): S (mol / L) \longrightarrow S (gm / L)

$$10^{-3}$$

$$S_{\text{Ag}_2\text{SO}_4} (\text{gm/L}) = 10^{-3} \times (108 \times 2 + 96)$$



Case (3): K_{sp} given , Solubility = ?



S 0 0

0 2S S



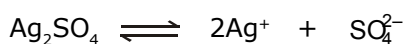
$$4S^3 = K_{sp}$$



$$S = 3 \sqrt{\frac{K_{sp}}{4}} \text{ mol/L}$$



Case (4): 70% of the dissolved salt ionizes .



S 0 0

$S - 0.7S$ $2 \times 0.7S$ $0.7S$



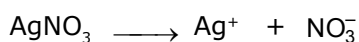
$$K_{sp} = (1.4S)^2 (0.7S)$$



$$S = 3 \sqrt{\frac{K_{sp}}{0.98}}$$

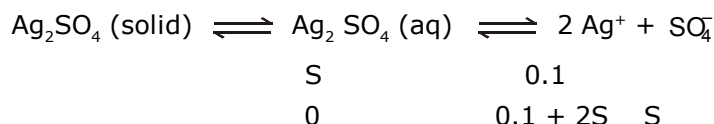


Case (5): Solubility of Ag_2SO_4 in 0.1 M AgNO_3



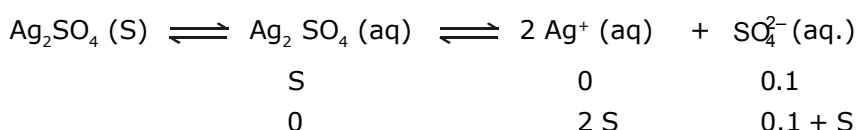
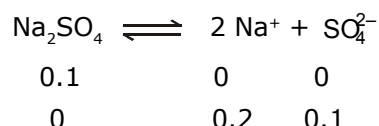
0.1 0 0

0 0.1 0.1



$$\Rightarrow K_{sp} = (0.1 + 2S)^2 (S) \Rightarrow K_{sp} \approx (0.1)^2 \times S \Rightarrow S = \frac{K_{sp}}{0.01}$$

☞ **Case (6) :** Solubility of Ag_2SO_4 in 0.1M Na_2SO_4



$$\Rightarrow K_{sp} = (2S)^2 (S + 0.1) \Rightarrow \approx 4S^2 \times 0.1 \Rightarrow S = \sqrt{\frac{K_{sp}}{0.4}}$$

☞ **Case (7) :** 100 ml 0.01 M AgNO_3 + 400 ml 0.02 M Na_2SO_4 , $K_{sp} (\text{Ag}_2\text{SO}_4) = 4 \times 10^{-9}$

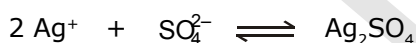
(a) Will any ppt or not ?

$$Q = [\text{Ag}^+]^2 [\text{SO}_4^{2-}] \quad Q = (1/500)^2 \left[\frac{8}{500} \right] = 6.4 \times 10^{-8} \quad Q > K_{sp} \Rightarrow \text{ppt}$$

(b) After ppt $[\text{Ag}^+] = ?$; $[\text{SO}_4^{2-}] = ?$
at equilibrium

$$4S^3 = 4 \times 10^{-9} \quad S = 10^{-3}$$

Number of moles of $(\text{Ag}_2\text{SO}_4) = 500 \times 10^{-3} = 0.5 \text{ m mole}$



1	8	
1 - 2x	8 - x	x

?

y	7.5	0.5	$\left(\frac{y}{500}\right)^2 \times \left(\frac{7.5}{500}\right) = K_{sp} = 4 \times 10^{-9}$	y = ?
---	-----	-----	--	-------

12. INDICATORS

Broadly defined, as indicator is substance which is used for the visual detection and determination of a specific constituent present in any sample. The visual observation used is primarily that of colour, but observations of fluorescence and turbidity are also used. Indicators under this general definition include all reagents which can be used in colorimetry, fluorimetry and turbidimetry. It is convenient, therefore, to define an indicator in a more limited way, as substance which is used for the visual detection of the completion of a particular reaction that is for the end point of a titration.

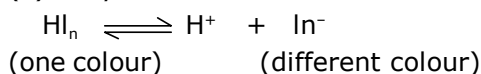
Acid-Base Indicators :- Acid-base indicators are organic substances which have one colour in acid solution while an altogether different colour in alkaline solution.

Theories of Acid-Base Indicators :-

Two important theories have been put forward to explain their behaviour:

(I) Ostwald's theory (1891) : According to this theory:

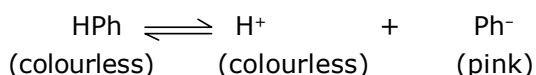
- (i) Acid- base indicators are weak organic acids or bases.
- (ii) They have different colours in ionised and non-ionised states i.e.



(iii) The colour of the indicator depends on the relative proportions of the unionised indicator molecules and its ions.

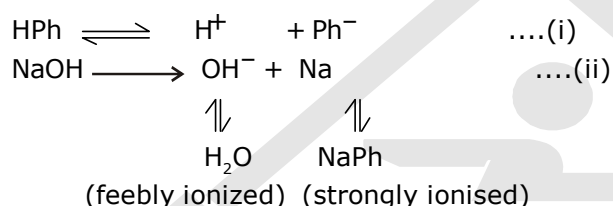
On the basis of above postulates. Ostwald explained the action of phenolphthalein, methyl orange, methyl red and other acid-base indicators.

(a) Action of Phenolphthalein:- Phenolphthalein is a weak acid (HPh) and is almost unionised. Its unionised molecules are colourless whilst on ionisation give colourless H^+ ions and pink coloured Ph^- ions.

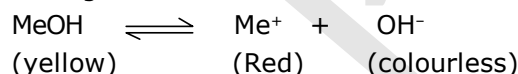


In the presence of acid due to increase in the concentration of common H^+ ions, the dissociation of HPh is suppressed and thus the solution becomes colourless.

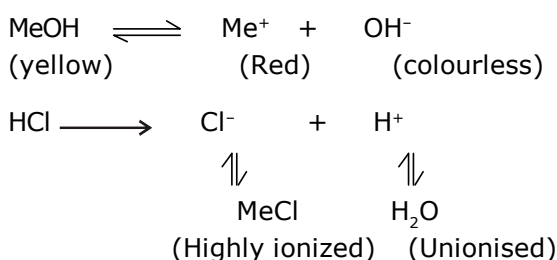
On the other hand, the addition of strong bases (like NaOH, KOH), however, the OH^- ions produced from them combine with the H^+ ions from the phenolphthalein to form feebly ionised water. The equilibrium (i) is thus disturbed and more of the phenolphthalein ionises to produce Ph^- ions. The latter combine with Na^+ ions to form the strongly ionised sodium salt NaPh and hence remains in the ionic state giving pink coloured Ph^- ions.



(b) Methyl orange :- It is a weak base and can be represented as MeOH. Its undissociated molecule is yellow while gives red coloured Me^+ ions on dissociation,

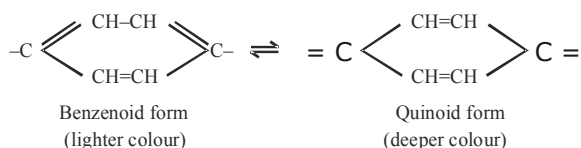


If a base (i.e., OH^- ions) is added to the indicator, the OH^- ions will suppress the ionisation of the indicator. Hence, the indicator will remain yellow in an alkali. However, if a small excess of acid (say, HCl) is added, the latter will force the equilibrium to the right by removing OH^- ions to form H_2O . This will result in the formation of red coloured Me^+ ions in the solution.



(II) Modern Quinoid Theory :- Main postulates of this theory are:

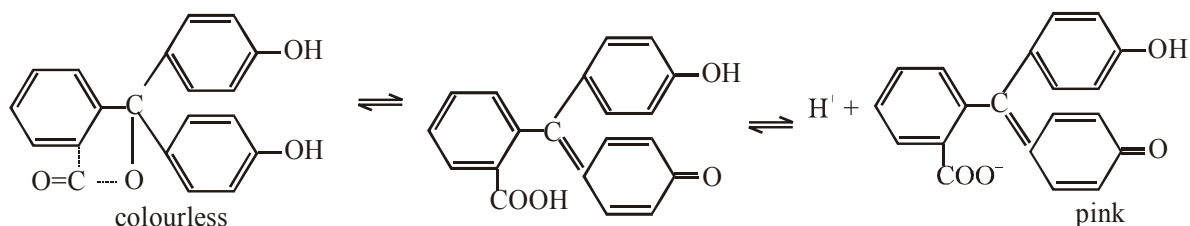
- (i) The indicators used in acid-alkali titrations are aromatic organic compounds which are equilibrium mixtures of at least two tautomeric forms, ordinarily one form is benzenoid while the other is quinoid.
- (ii) The two forms have different colours. The quinoid form is usually deeper in colour than the benzenoid form. Out of these one form exists in acidic solution while other in alkaline solution.



- (iii) Change in pH causes the transition of benzenoid form to quinoid form and vice versa and consequently a change in colour.

This theory explains the action of phenolphthalein, methyl orange and other acid-base indicators.

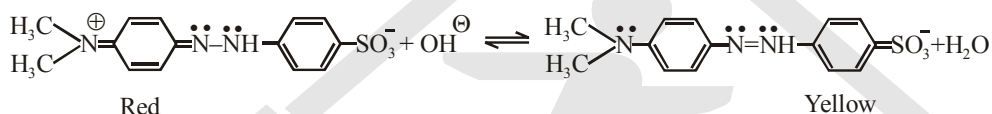
- (a) **Action of Phenolphthalein:-** Phenolphthalein is an acidic indicator undergoing the following transformation:



In alkaline medium, OH^- ions combine with H^+ ions produced by the indicator, the equilibrium shifts to the right producing pink colour. In acid medium the dissociation of the organic acid is suppressed, the equilibrium shifts to the left and the solution becomes colourless.

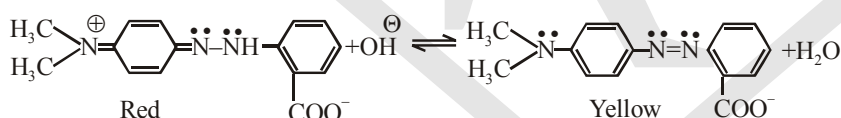
(b) Action of Methyl Orange

Methyl orange is a basic indicator. More correctly it is an amphoteric compound containing both acidic group $-\text{SO}_3\text{H}$ and basic group $-\text{N}(\text{CH}_3)_2$. The quinoid form (red) combines with the OH^- ions in alkaline medium favouring the formation of yellow.



(c) Action of Methyl Red

Methyl red is a basic indicator and the colour change takes place according to the following scheme:



Acid-Base Indicators with pH range of colour change

Indicator	Colour in acid	Colour in alkali	pH range of colour change
Methyl orange	Red	Yellow	3.2 - 4.4
Bromo-cresol green	Yellow	Blue	3.8 - 5.4
Methyl red	Yellow	Red	4.8 - 6.0
Bromothymol blue	Yellow	Blue	6 - 7.5
Phenol red	Yellow	Red	6.3 - 8.4
Phenolphthalein	Colourless	Pink	8.2 - 10
Thymol blue	Yellow	Blue	8 - 9.6
Thymolphthalein	Colourless	Blue	9.4 - 10.6

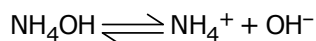
Choice of Indicators:-

At the equivalence point of acid- base titration there occurs a sudden jump in pH of the solution. An indicator, the pH range of colour change of which falls within this limit, is suitable and is used in that titration. No sudden pH jump of the solution in the titration of weak acid with weak base occurs and so no indicator is suitable for this titration.

	Nature of Titration	pH Jump at the Equivalence point	Suitable Indicator
1.	Strong acid and strong base	4-10	Any Indicator (Methyl orange, Methyl red, Phenolphthalein, Bromo thymol blue etc.)
2.	Weak acid and strong base	6.5 - 10	Phenolphthalein, Thymol blue, Thymolphthalein
3.	Strong acid and weak base	4 - 7.5	Methyl orange, Methyl red, Bromocresol green
4.	Weak acid and weak base	—	No indicator is suitable

Sol. (C)

NH_4OH is a weak base and partially dissociated



Concentration 1 0 0
before dissociation

Concentration $1 - \alpha$ α α
after dissociation

$$\therefore [\text{OH}^-] = C\alpha = 2 \times 10^{-3}$$

$$\times \frac{2}{100} = 4 \times 10^{-5} \text{ M}$$

$$\text{pOH} = -\log[\text{OH}^-]$$

$$= -\log 4 \times 10^{-5} = 4.4$$

$$\text{pH} = 14 - 4.4$$

$$= 9.6$$

Ex.7 How many hydrogen ions are present in 1 ml of a solution of pH = 13 –

- (A) 6.02×10^{13} (B) 6.02×10^{12}
(C) 6.02×10^7 (D) 6.02×10^5

Sol. (C)

$$\text{pH} = 13$$

$$-\log [\text{H}^+] = 13$$

$$\text{or } [\text{H}^+] = 10^{-13} \text{ mole/litre}$$

$$[\text{H}^+] \text{ in 1 ml} = 10^{-16} \text{ moles}$$

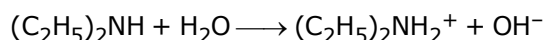
$$1 \text{ mole } \text{H}^+ \text{ contains } 6.023 \times 10^{23} \text{ H}^+ \text{ ions}$$

$$\therefore \text{No. of } \text{H}^+ \text{ ions in } 10^{-16} \text{ moles}$$

$$= 6.023 \times 10^{23} \times 10^{-16} = 6.023 \times 10^7$$

Ex.8 The pH of 0.05 M aqueous solution of diethyl amine is 12.0 Calculate K_b .

Sol. Diethyl amine is base and gives OH^- as,



Initial conc. 1 0 0

Equilibrium conc. ($1 - \alpha$) α α

$$\therefore [\text{OH}^-] = C\alpha$$

where C is conc. of bas and $C = 0.05 \text{ M}$

$$\therefore \text{pH} = 12 \quad \therefore \text{pOH} = 2$$

$$\text{or } [\text{OH}^-] = 10^{-2} \text{ M}$$

$$\therefore C\alpha = 10^{-2}$$

$$\text{or } 0.05 \times \alpha = 10^{-2} \quad (\because C = 0.05)$$

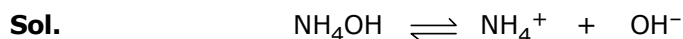
$$\alpha = 0.2$$

$$\text{Now for a base, } K_b = \frac{C\alpha^2}{(1-\alpha)} = \frac{0.05 \times (0.2)^2}{(1-0.2)}$$

$$= \frac{0.05 \times 0.04}{0.8} = 2.5 \times 10^{-3}$$

Note : Do not use $K_b = C\alpha^2$ since $\alpha = 0.2$ and $1 - \alpha = 0.8$

Ex.9 A solution of 0.01 M concentration of NH_4OH is 2.6% dissociated. Calculate $[\text{H}^+]$, $[\text{OH}^-]$, $[\text{NH}_4^+]$, $[\text{NH}_4\text{OH}]$ and pH of solution.



Before dissociation 1 0 0

After dissociation $1 - \alpha$ α α

$$\therefore [\text{OH}^-] = C\alpha = C\sqrt{K_b/C} = \sqrt{K_b C}$$

$$\text{Also } K_b = C\alpha^2 = 0.01 \times (0.026)^2 = 6.76 \times 10^{-6}$$

$$\therefore [\text{OH}^-] = \sqrt{[6.76 \times 10^{-6} \times 0.01]} = 2.6 \times 10^{-4} \text{ M}$$

$$\therefore [\text{H}^+] = 10^{-14}/2.6 \times 10^{-4}$$

$$= 3.846 \times 10^{-11} \text{ M}$$

$$\therefore \text{pH} = -\log [\text{H}^+] = -\log 3.846 \times 10^{-11}$$

$$= 10.415$$

Ex.10 The pH of a 0.05 M solution of H_2SO_4 in water is nearly –

- (A) 0.05 (B) 1
(C) -1 (D)

Sol. (B)

$$\text{pH} = -\log_{10} [\text{H}^+]$$

The concentration of H^+ ions is expressed in gm equivalent

$$\text{Molarity of } \text{H}_2\text{SO}_4 = 0.05$$

$$\therefore \text{Normality} = 0.05 \times 2 = 0.1$$

$$\therefore \text{pH} = -\log 0.1$$

$$\text{or pH} = 1$$

Ex.11 Calculate the pH of solution having H^+ ion concentration of $5 \times 10^{-4} \text{ mole/litre}$ –

- (A) 3.3 (B) 2.26
(C) 1.26 (D) 0.26

Sol. (A)

$$[\text{H}^+] \text{ ion concentration} = 5 \times 10^{-4} \text{ mole/litre}$$

$$\text{pH} = -\log [5 \times 10^{-4}]$$

$$= -(\log 5 + \log 10^{-4})$$

$$= -0.7 + 4$$

$$= 3.3$$

Ex.12 The dissociation constant of weak acid HA is 4.9×10^{-8} . After making the necessary approximations. Calculate pH in 0.1 M acid -

(A) 1.155 (B) 2.155

(C) 3.155 (D) 4.155

Sol. (D)

For weak acid $K_a = \alpha^2.C$

$$\therefore \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{4.9 \times 10^{-8}}{0.1}}$$

$$= 7 \times 10^{-4}$$

$$\text{pH} = -\log H^+ = -\log \alpha C$$

$$= -\log 7 \times 10^{-4} \times 10^{-1}$$

$$= 4.1549 = 4.155$$

Ex.13 Calculate the pH of solution obtained by mixing 10 ml of 0.1M HCl and 40ml. of 0.2M H_2SO_4 -

(A) 0.3685 (B) 0.4685

(C) 1.3685 (D) 1.4684

Sol. (B)

Milli equivalent of H^+ from HCl = $10 \times 0.1 = 1$

Milli equivalent of H^+ from H_2SO_4

$$= 40 \times 0.2 \times 2 = 16$$

Total Meq of H^+ in solution = $1 + 16 = 17$

$$[H^+] = \frac{17}{50} = 3.4 \times 10^{-1} \quad [\therefore [H^+] = \frac{\text{Meq}}{V_{\text{in ml}}}]$$

$$\text{pH} = -\log [H^+] = -\log [0.34] = 0.4685$$

Ex.14 Find the pH of solution prepared by mixing 25ml of a 0.5 M solution of HCl, 10ml of a 0.5 M solution of NaOH and 15ml of water -

(A) 0.8239 (B) 1.0029

(C) 1.0239 (D) 1.8239

Sol. (A)

We know that for HCl and NaOH, m.e. = m.e.

$$\therefore \text{m.e. of HCl} = 0.5 \times 25 = 12.5$$

$$\text{m.e. of NaOH} = 0.5 \times 10 = 5.0$$

m.e. of HCl in the resultant mixture

$$= 12.5 - 5.0 = 7.5$$

$$\text{total volume} = (25 + 10 + 15) \text{ ml} = 50 \text{ ml}$$

$$\therefore \text{Normally of HCl} = \frac{\text{m.e.}}{\text{Vol(ml)}} = \frac{7.50}{50}$$

$$\therefore \text{Molarity} = \frac{7.50}{50}$$

$$\therefore [H^+] = [HCl] = \frac{7.50}{50}$$

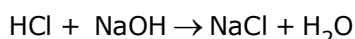
$$\therefore \text{pH} = -\log \frac{7.50}{50} = 0.8239$$

Ex.15 Calculate the pH of a solution which contains 10 ml of 1M HCl and 10 ml of 2 M NaOH

(A) 11.7 (B) 12.7

(C) 13.7 (D) 10.7

Sol. (C)



Meq. before 10×1 10×2

Reaction = 10 = 20 0 0

Meq. After 0 10 10 10

Reaction

$$[OH^-] \text{ left from NaOH} = \frac{10}{20} = 0.5 \text{ M}$$

$$\text{pOH} = -\log OH^- = -\log 0.5$$

$$\text{pOH} = 0.3$$

$$\text{pH} = 13.7$$

Ex.16 Saccharin ($K_a = 2 \times 10^{-12}$) is a weak acid respectively by formula HSaC. A 4×10^{-4} mole amount of Saccharin is dissolved in 200cc water of pH 3. Assuming no change in volume. Calculate the concentration of Sac. ions in the resulting solution at equilibrium -

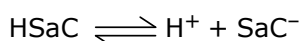
(A) 2×10^{-12} M (B) 3×10^{-12} M

(C) 4×10^{-12} M (D) 5×10^{-12} M

Sol. (C)

$$[\text{HSaC}] = \frac{4 \times 10^{-4}}{200/1000} = 2 \times 10^{-3} \text{ M}$$

The dissociation of HSaC takes places in the presence of $[H^+] = 10^{-3}$



conc. before 2×10^{-3} 10^{-3} 0

dissociation

In presence of H^+ the dissociation of HSaC is almost negligible because of common ion ef-

fect. Thus at equilibrium

$$[\text{HSaC}] = 2 \times 10^{-3}, \text{H}^+ = 10^{-3}$$

$$K_a = \frac{[\text{H}^+][\text{SaC}^-]}{[\text{HSaC}]}$$

$$\therefore 2 \times 10^{-12} = \frac{[10^{-3}][\text{SaC}^-]}{[2 \times 10^{-3}]}$$

$$\therefore [\text{SaC}^-] = 4 \times 10^{-12} \text{ M}$$

Ex.17 Calculate pH of a solution whose 100 ml contains 0.2 gm NaOH dissolved in it -

- (A) 10.699 (B) 11.699
(C) 12.699 (D) 13.699

Sol. (C)

100ml solution of NaOH contains
= 2.0gm NaOH

\therefore 1000 ml solution of NaOH contains
= 2 gm NaOH

$$\text{Normality of solution} = \frac{2}{40} = 0.05 \text{ N}$$

$$\therefore [\text{H}^+] = \frac{10^{-14}}{0.05}$$

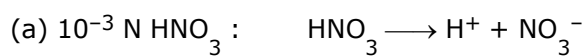
$$\therefore -\log[\text{H}^+] = -\log \left[\frac{10^{-14}}{0.05} \right]$$

$$= -[-14 + 2 - 0.6990] = \mathbf{12.699}$$

Ex18 Calculate pH of -

- (a) 10^{-3} N HNO_3 , (b) $10^{-3} \text{ M H}_2\text{SO}_4$,
(c) $10^{-3} \text{ N H}_2\text{SO}_4$, (d) 0.01 N HCl ,
(e) 10^{-8} N HCl (f) 10^2 M HCl .

Sol. Strong acids ionize completely at normal dilutions



Conc. before ionisation 10^{-3} N 0 0

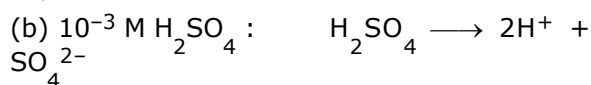
Conc. after ionisation 0 10^{-3}
 10^{-3}

$$\therefore [\text{H}^+] = 10^{-3} \text{ mol/litre or eq./litre}$$

(H^+ is monovalent)

$$\therefore \text{pH} = -\log [\text{H}^+] = -\log 10^{-3}$$

$$\therefore \text{pH} = 3$$



Conc. before ionisation 10^{-3} M 0 0

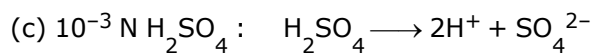
Conc. after ionisation 0 2×10^{-3} 10^{-3}

Mole ratio of $\text{H}_2\text{SO}_4 : \text{H}^+ : \text{SO}_4^{2-} :: 1 : 2 : 1$

$$[\text{H}^+] = 2 \times 10^{-3} \text{ M}$$

$$\therefore \text{pH} = -\log [\text{H}^+] = -\log 2 \times 10^{-3}$$

$$\therefore \text{pH} = 2.6989$$



Conc. before ionisation 10^{-3} N 0 0

Conc. after ionisation 0 10^{-3} 10^{-3}

\therefore Equal equivalent of a substance gives equal equivalent of its components.

$$\therefore [\text{H}^+] = 10^{-3} \text{ M}$$

$$\text{pH} = -\log [\text{H}^+]$$

$$\therefore \text{pH} = 3$$



Conc. before ionisation 10^{-2} N 0 0

Conc. after ionisation 0 10^{-2}
 10^{-2}

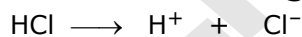
$$[\text{H}^+] = 10^{-2} \text{ M}$$

$$\therefore \text{pH} = -\log [\text{H}^+]$$

$$\therefore \text{pH} = 2$$

(e) 10^{-8} N HCl :

Solution I :



Conc. before ionisation 10^{-8} N 0 0

Conc. after ionisation 0 10^{-8} 10^{-8}

$\therefore [\text{H}^+] = 10^{-8} \text{ M}$ but $\text{pH} = 8$ is not possible because it is acid. Now $[\text{H}^+] = 10^{-7} \text{ M}$ are already present in solution and since $10^{-8} < 10^{-7}$ and thus, it should not be neglected.

$$\therefore [\text{H}^+] = 10^{-8} + 10^{-7} = 1.1 \times 10^{-7} \text{ M}$$

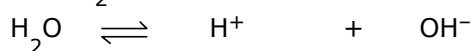
$$\text{pH} = 1.1 \times 10^{-7} \text{ M}$$

$$\therefore \text{pH} = 6.9586$$

Solution II :

The above solution lacks with discrepancy that dissociation of H_2O , weak electrolyte is also suppressed in presence of HCl due to common ion effect and thus, $[\text{H}^+]_{\text{H}_2\text{O}}$ but will be lesser than 10^{-7} .

Therefore, dissociation of H_2O in presence of 10^{-8} H_2^+ .



$$(10^{-8} + a) \quad a$$

$$\therefore K_w = (10^{-8} + a) a$$

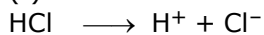
$$a = 0.95 \times 10^{-7}$$

$$\therefore [H^+] = 10^{-8} \times 0.95 \times 10^{-7}$$

$$= 1.05 \times 10^{-7}$$

$$\therefore \text{pH} = 6.9788$$

(f) 10^2 M HCl :



$$\text{Conc. before dissociation} \quad 10^2 \text{ M} \quad 0 \quad 0$$

$$\text{Conc. after dissociation} \quad 0 \quad 10^2 \quad 10^2$$

$$\therefore [H^+] = 10^2 \text{ M}$$

$$\therefore \text{pH} = -2$$

But this is not true. This may be explained as follows :

Sorenson's originally intended pH to be related to $[H^+]$, but his fundamental method of measurement – the hydrogen electrode – is now known to depend on thermodynamics activities rather than $[H^+]$, i.e., on $\log a_{H^+} = [H^+]f_{H^+}$.

In dilute solutions f_{H^+} is near enough to unity and thus, $a_{H^+} = [H^+]$. Thus, pH defined by $-\log [H^+]$ is not only of little theoretical significance, but in fact cannot be measured directly. It has therefore, come to be accepted that $\text{pH} = -\log_{10} a_{H^+}$, i.e., pH of 10^2 M HCl cannot be calculated and it practically lies near to zero.

Ex.19 Which of the following has pH is equal to near about one -

(A) $100 \text{ ml } \frac{\text{M}}{10} \text{ HCl} + 100 \text{ ml } \frac{\text{M}}{10} \text{ NaOH}$

(B) $55 \text{ ml } \frac{\text{M}}{10} \text{ HCl} + 44 \text{ ml } \frac{\text{M}}{10} \text{ NaOH}$

(C) $10 \text{ ml } \frac{\text{M}}{10} \text{ HCl} + 90 \text{ ml } \frac{\text{M}}{10} \text{ NaOH}$

(5) $75 \text{ ml } \frac{\text{M}}{5} \text{ HCl} + 25 \text{ ml } \frac{\text{M}}{5} \text{ NaOH}$

Sol. (D)

$$25 \text{ ml } \frac{\text{M}}{5} \text{ NaOH will be neutralise } 25 \text{ ml } \frac{\text{M}}{5} \text{ HCl.}$$

Hence, $50 \text{ ml } \frac{\text{M}}{5} \text{ HCl}$ get rest and to the mixing of both solution will give total 100 ml volume.

$$N_1 V_1 = N_2 V_2$$

$$50 \times \frac{N}{5} = N_2 \times 100$$

$$N_2 = \frac{50 \times N}{5 \times 100} = .1 \text{ Hence, } \text{pH} = 1$$

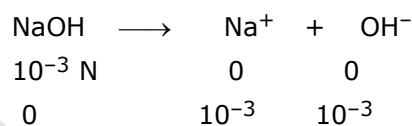
Ex.20 Calculate pH for -

(a) 0.001 N NaOH , (b) 0.01 N Ca(OH)_2 ,

(c) 0.01 M Ca(OH)_2 , (d) 10^{-8} M NaOH ,

(e) 10^2 M NaOH , (f) $0.0008 \text{ M Mg(OH)}_2$

Sol. (a) 0.001 N NaOH :



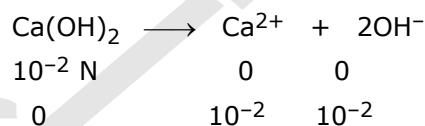
$$\therefore [\text{OH}^-] = 10^{-3} \text{ M}$$

$$\therefore \text{pOH} = -\log [\text{OH}^-] = -\log 10^{-3} = 3$$

$$\therefore \text{pH} = 14 - \text{pOH} = 14 - 3 = 11$$

$$\therefore \text{pH} = 11$$

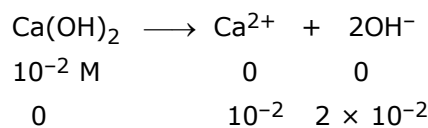
(b) 0.01 N Ca(OH)_2 :



$$\therefore [\text{OH}^-] = 10^{-2} \text{ M}$$

$$\therefore \text{pOH} = 2 \quad \therefore \text{pH} = 12$$

(c) 0.01 M Ca(OH)_2 :

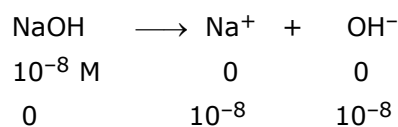


$$[\text{OH}^-] = 2 \times 10^{-2} \text{ M}$$

$$\therefore \text{pOH} = 1.6989$$

$$\therefore \text{pH} = 14 - 1.6989 = 12.3010$$

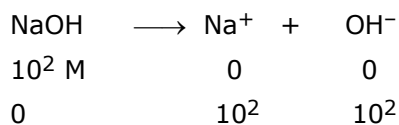
(d) 10^{-8} M NaOH :



$$\therefore [\text{OH}^-] = 10^{-8} \text{ M}$$

Now proceed for OH^- as in problem 50 part (e)

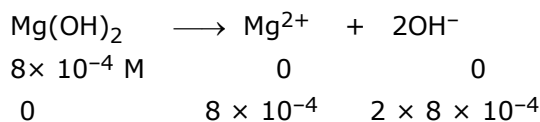
(e) 10^2 M NaOH :



$$\therefore [\text{OH}^-] = 10^2 \text{ M}$$

Now proceed as in Problem 50 part (f).

(f) $0.0008 \text{ M Mg (OH)}_2$:



$$\therefore [\text{OH}^-] = 16 \times 10^{-4} \text{ M}$$

$$\therefore \text{pOH} = 2.7958$$

$$\therefore \text{pH} = 11.2041$$

Ex.21 If 0.561 g KOH is dissolved in water to give 200 mL of solution at 298 K. Calculate the concentrations of potassium, hydrogen and hydroxyl ions. What is its pH ?

Sol. $\text{KOH} \longrightarrow \text{K}^+ + \text{OH}^-$

$$[\text{KOH}] = \frac{0.561 \times 1000}{56 \times 200} = 5.01 \times 10^{-2} \text{ M}$$

$$\therefore [\text{OH}^-] = 5.01 \times 10^{-2} \text{ M}$$

$$\begin{aligned} \text{or } \text{pOH} &= -\log [\text{OH}^-] = -\log 5.01 \times 10^{-2} \\ &= 1.3002 \quad \therefore \text{pH} = 12.6998 \end{aligned}$$

$$[\text{H}^+] = 1.996 \times 10^{-13}; [\text{K}^+] = 5.01 \times 10^{-2}$$

Ex.22 Calculate the hydrogen ion concentration in the following biological fluids whose pH are given below -

- Human muscle-fluid 6.86
- Human stomach fluid 1.2
- Human blood 7.38
- Human saliva 6.4

Sol. (a) $\text{pH} = 6.83$ or $-\log [\text{H}^+] = 6.83$

$$\therefore [\text{H}^+] = 1.479 \times 10^{-7} \text{ M}$$

(b) $\text{pH} = 1.2$ or $-\log [\text{H}^+] = 1.2$

$$\therefore [\text{H}^+] = 6.319 \times 10^{-2} \text{ M}$$

(c) $\text{pH} = 7.38$ or $-\log [\text{H}^+] = 7.38$

$$\therefore [\text{H}^+] = 4.17 \times 10^{-8} \text{ M}$$

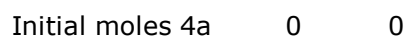
(d) $\text{pH} = 6.4$ or $-\log [\text{H}^+] = 6.4$

$$\therefore [\text{H}^+] = 3.98 \times 10^{-7} \text{ M}$$

Ex.23 How many mole of Ca(OH)_2 must be dissolved to produce 250 mL of an aqueous solution of pH 10.65, assuming complete dissociation ?

Sol. Let a mole of Ca(OH)_2 be dissolved in 250 mL solution to have $\text{pH} = 10.65$

$$[\text{Ca(OH)}_2] = \frac{a \times 1000}{250} = 4a \text{ M}$$



$$\therefore [\text{OH}^-] = 8a \text{ M}$$

$$[\text{H}^+] = \frac{10^{-14}}{8a}$$

$$\therefore \text{pH} = -\log [\text{H}^+]$$

$$\therefore 10.65 = -\log \frac{10^{-14}}{8a}$$

$$\frac{10^{-14}}{8a} = 2.238 \times 10^{-11}$$

$$\therefore a = 5.58 \times 10^{-5} \text{ mole}$$

Ex.24 Calculate K for the $\text{A}^- + \text{H}_3\text{O}^+ \rightleftharpoons \text{HA} + \text{H}_2\text{O}$ if K_a value for the acid HA is 1.0×10^{-6} .

Sol. $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{A}^- + \text{H}_3\text{O}^+$, $K_a = 1.0 \times 10^{-6}$

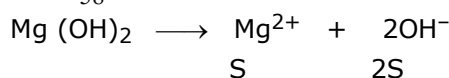
$$\text{Thus } K = \frac{1}{K_a} = 1.0 \times 10^6$$

Ex.25 The solubility of Mg(OH)_2 in pure water is $9.57 \times 10^{-3} \text{ g litre}^{-1}$. Calculate the pH of its saturated solution. Assume 100% ionization.

Sol. Solubility of Mg(OH)_2 in pure water

$$= 9.47 \times 10^{-3} \text{ g/litre}$$

$$= \frac{9.57 \times 10^{-3}}{58} \text{ mole litre} = 1.65 \times 10^{-4} \text{ M}$$



$$\therefore [\text{OH}^-] = 2 \times [\text{Mg(OH)}_2]$$

$$= 2 \times 1.65 \times 10^{-4} = 3.3 \times 10^{-4}$$

$$\therefore \text{pOH} = -\log [\text{OH}^-] = 3.48$$

$$\therefore \text{pH} = 14 - 3.48 = 10.52$$

Ex.26 A solution of HCl has a pH = 5. If one mL of it is diluted to 1 litre, what will be the pH of resulting solution ?

Sol. Meq. of HCl_I in mL = $10^{-5} \times 1$

$$\text{Meq. of } \text{HCl}_{II} \text{ in } 1000 \text{ mL} = N \times 1000$$

Since II is prepared by diluting I and Meq. does not change on dilution

i.e. Meq of HCl (conc.) = Meq. of HCl (dil.)

$$\therefore 10^{-5} \times 1 = N \times 1000$$

$$\therefore N_{\text{HCl}_{\text{II}}} = 10^{-8}$$

Now proceed as Problem 50 part (e)

$$\therefore \text{pH} = 6.9788$$

Ex.27 Calculate the pH of a solution of given mixtures;

(a) (4g CH_3COOH + 6 g CH_3COONa) in 100 mL of mixture;

$$K_a \text{ for } \text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$$

(b) 5 mL of 0.1 M BOH + 250 mL of 0.1 M BCl;

$$K_b \text{ for } \text{MOH} = 1.8 \times 10^{-5}$$

(c) (0.25 mole of CH_3COOH + 0.35 mole of CH_3COONa) in 500 mL mixture;

$$K_a \text{ for } \text{CH}_3\text{COOH} = 3.6 \times 10^{-4}$$

Sol. (a) We have $\text{pH} = -\log K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$

$$\therefore [\text{salt}] = \frac{6 \times 1000}{82 \times 100} \text{ M and } [\text{acid}] = \frac{4 \times 1000}{60 \times 100} \text{ M}$$

$$\therefore \text{pH} = -\log 1.8 \times 10^{-5} + \log \frac{6 \times 1000 / 82 \times 100}{4 \times 1000 / 60 \times 100}$$

$$\therefore \text{pH} = 4.7851$$

$$(b) \text{pOH} = -\log K_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$\therefore \text{Total volume after mixing} = 250 + 5 = 255 \text{ mL}$$

$$\text{Meq. of salt} = 250 \times 0.1 = 25$$

$$\text{Meq. of base} = 5 \times 0.1 = 0.5$$

$$\therefore [\text{salt}] = \frac{25}{255} \text{ and } [\text{base}] = \frac{0.5}{255}$$

$$\therefore \text{pOH} = -\log 1.8 \times 10^{-5} + \log \frac{25/255}{0.5/255}$$

$$\text{pOH} = 6.4437$$

$$\therefore \text{pOH} = 14 - \text{pOH} = 7.5563$$

$$(c) \text{pH} = -\log K_b + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

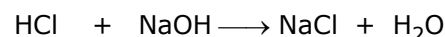
$$= -\log 3.6 \times 10^{-4} + \log \frac{0.35/500}{0.25/500}$$

$$\text{pH} = 3.5898$$

Ex.28 What will be the resultant pH when 200 mL of an aqueous solution of HCl (pH = 2.0) is mixed with 300 mL of an aqueous solution of NaOH (pH = 12.0) ?

$$\text{Sol. pH of HCl} = 2 \quad \therefore [\text{HCl}] = 10^{-2} \text{ M}$$

$$\text{pH of NaOH} = 12 \quad \therefore [\text{NaOH}] = 10^{-2} \text{ M}$$



$$\text{Meq. before reaction} \quad 200 \times 10^{-2} \quad 300 \times 10^{-2} \quad 0 \quad 0$$

$$\text{Meq. after reaction} \quad = 2 \quad = 3 \quad 2 \quad 2$$

$$\therefore [\text{OH}^-] \text{ left from NaOH} = \frac{1}{500} = 2 \times 10^{-3} \text{ M}$$

$$\therefore \text{pOH} = -\log \text{OH}^- = -\log 2 \times 10^{-3}$$

$$\therefore \text{pOH} = 2.6989$$

$$\therefore \text{pH} = 11.3010$$

Ex.29 10^{-6} M HCl is diluted to 100 times. Its pH is -

(A) 6.0

(B) 8.0

(C) 6.95

(D) 9.5

Sol. (C)

$$\text{New concentration of ; HCl} = \frac{10^{-6}}{100} = 10^{-8} \text{ M}$$

But HCl is acid and calculated pH by $\text{H}^+ = 10^{-7} + 10^{-8}$

Ex.30 The K_w for $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$ changes from 10^{-14} at 25°C to 9.62×10^{-14} at 60°C . What is pH of water at 60°C ? What happens to its neutrality?

Sol. K_w for H_2O at $25^\circ\text{C} = 10^{-14}$

$$\therefore [\text{H}^+][\text{OH}^-] = 10^{-14} \quad (\because K_w = [\text{H}^+][\text{OH}^-])$$

$$\therefore [\text{H}^+] = 10^{-7} \text{ M} \quad \therefore \text{pH} = 7$$

$$\text{Now } K_w \text{ for } \text{H}_2\text{O} \text{ at } 60^\circ\text{C} = 9.62 \times 10^{-14}$$

$$\therefore [\text{H}^+][\text{OH}^-] = 9.62 \times 10^{-14}$$

For pure water $[\text{H}^+] = [\text{OH}^-]$

$$\therefore [\text{H}^+]^2 = 9.62 \times 10^{-14}$$

$$\therefore [\text{H}^+] = \sqrt{9.62 \times 10^{-14}} = 3.10 \times 10^{-7} \text{ M}$$

$$\therefore \text{pH} = -\log \text{H}^+ = -\log 3.10 \times 10^{-7}$$

$$\therefore \text{pH} = 6.51$$

Thus, pH of water becomes 6.51 at 60° but the nature is neutral since calculation for pure water has been made, i.e., pH scale at 60°C becomes in between 0 to 13.02.

Ex.31 Calculate the pH of the resultant mixtures :

- (a) 10 mL of 0.2 M Ca(OH)_2 + 25 mL of 0.1 M HCl,
 (b) 10 mL of 0.01 M H_2SO_4 + 10 mL of 0.01 M Ca(OH)_2 ,
 (c) 10 mL of 0.1 M H_2SO_4 + 10 mL of 0.1 M KOH

Sol. (a) Meq. of $\text{Ca(OH)}_2 = 10 \times 0.2 \times 2 = 4$

Meq. of HCl = $25 \times 0.1 \times 1 = 2.5$

$$\left[\begin{array}{l} \text{Meq.} = N \times V_{\text{mL}} \\ = M \times \text{Valance factor} \times V_{\text{mL}} \end{array} \right]$$

\therefore Meq. of Ca(OH)_2 left = $4 - 2.5 = 1.5$

$\therefore N\text{Ca(OH)}_2 = \frac{1.5}{10+25} = 4.29 \times 10^{-2}$

$\therefore [\text{OH}^-] = 4.29 \times 10^{-2}$

$\therefore \text{pOH} = 1.3675 \quad \therefore \text{pH} = 12.6325$

(b) Meq. of $\text{H}_2\text{SO}_4 = 10 \times 0.01 \times 2 = 0.2$

\therefore Meq. of $\text{Ca(OH)}_2 = 10 \times 0.01 \times 2 = 0.2$

Solution is neutral and pH = 7

(c) Meq. of $\text{H}_2\text{SO}_4 = 10 \times 0.1 \times 2 = 2$

Meq. of KOH = $10 \times 0.1 \times 1 = 1$

$\therefore \text{NH}_2\text{SO}_4 = 1/20 = 5 \times 10^{-2}$

$\therefore [\text{H}^+] = 5 \times 10^{-2}$ and pH = 1.3010

Ex.32 20 ml of 0.2 M NaOH is added to 50 ml, of 0.2 M CH_3COOH to give 70ml, of the solution. What is the pH of the solution ? The ionization constant of acetic acid is 2×10^{-5} -

- (A) 4.522 (B) 5.568
 (C) 6.522 (D) 7.568

Sol. (A)

The addition of NaOH converts equivalent amount of acetic acid into sodium acetate. Hence,

Concen. of acetic acid after the addition of

$$\text{NaOH} = \frac{30}{70} \times 0.2 \text{ M}$$

Concen. of CH_2COONa after the addition of

$$\text{NaOH} = \frac{20}{70} \times 0.2 \text{ M}$$

Hense, Using the expression

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= -\log (2 \times 10^{-5}) + \log \left(\frac{20}{30} \right)$$

$$= 4.699 - 0.177 = \mathbf{4.522}$$

Ex.33 The ionization constant of propionic acid is 1.32×10^{-5} . Calculate the degree of ionization of the acid in its 0.05 M solution and also its pH. What will be its degree of ionization in the solution of 0.01 N HCl ?

Sol. $\text{CH}_3\text{CH}_2\text{COOH} \rightleftharpoons \text{CH}_3\text{CH}_2\text{COO}^- + \text{H}^+$
 $c(1-\alpha) \quad \quad \quad c\alpha \quad \quad \quad c\alpha$

$$K_a = 1.32 \times 10^{-5} = \frac{[\text{CH}_3\text{CH}_2\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{CH}_2\text{COOH}]}$$

$$= \frac{c\alpha \cdot c\alpha}{c(1-\alpha)} = c\alpha^2 (\because 1-\alpha \approx 1)$$

$$\therefore 0.05 \times \alpha^2 = 1.32 \times 10^{-5} ; \alpha = 1.63 \times 10^{-2}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(c\alpha)$$

$$= -\log(0.05 \times 1.36 \times 10^{-2}) = 3.09$$

In 0.01 N HCl, $[\text{H}^+] = 0.01$ and thus

$$1.32 \times 10^{-5} = \frac{c\alpha \times 0.01}{c(1-\alpha)} = \alpha \times 0.01 (1-\alpha \approx 1)$$

$$\therefore \alpha = 1.32 \times 10^{-3}$$

Ex.34 Determine degree of dissociation of 0.05 M NH_3 at 25°C in a solution of pH = 11.

Sol. $\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$
 $1 \quad \quad \quad 0 \quad \quad \quad 0$
 $c(1-\alpha) \quad \quad \quad c\alpha \quad \quad \quad c\alpha$

Given pH = 11

$$\therefore [\text{H}^+] = 10^{-11} \quad [\because [\text{H}^+][\text{OH}^-] = 10^{-14}]$$

$$[\text{OH}^-] = 10^{-3} = c\alpha$$

Since, $c = 0.05$

$$\therefore \alpha = \frac{10^{-3}}{c} = \frac{10^{-3}}{0.05} = 2 \times 10^{-2} \quad \text{or} \quad 2\%$$

Ex.35 How many mole of NH_4Cl must be added to one litre of 1.0 M NH_4OH to have a buffer of pH = 9. $K_{\text{NH}_4\text{OH}} = 1.8 \times 10^{-5}$?

Sol. For Basic buffer solutions

$$\text{pOH} = -\log K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

Let a mole of NH_4Cl are added to (1.0×1) mole of NH_4OH in 1 litre.

Given pH = 9 \therefore pOH = 5

$$\therefore 5 = -\log 1.8 \times 10^{-5} + \log \frac{a}{1.0 \times 1}$$

or $a = 1.8$

Ex.36 A solution contains 0.1 M H_2S and 0.3 M HCl. Calculate the conc. of S^{2-} and HS^- ions in solution. Given K_{a_1} and K_{a_2} for H_2S are 10^{-7} and 1.3×10^{-13} respectively.

Sol. $\text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^- \quad K_{a_1} = 10^{-7}$

$\text{HS}^- \rightleftharpoons \text{H}^+ + \text{S}^{2-} \quad K_{a_2} = 1.3 \times 10^{-13}$

Due to common ion effect the dissociation of H_2S is suppressed and the $[\text{H}^+]$ in solution is due to HCl

$$\therefore K_{a_1} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}$$

$$10^{-7} = \frac{[0.3][\text{HS}^-]}{[0.1]} \quad [\because [\text{H}^+] \text{ from HCl} = 0.3]$$

$$\therefore [\text{HS}^-] = \frac{10^{-7} \times 0.1}{0.3}$$

$$= 3.3 \times 10^{-8} \text{ M}$$

$$\text{Further } K_{a_2} = \frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]} \text{ and } K_{a_1} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}$$

$$\therefore K_{a_1} \times K_{a_2} = \frac{[\text{H}^+][\text{S}^{2-}]}{[\text{H}_2\text{S}]}$$

$$10^{-7} \times 1.3 \times 10^{-13} = \frac{[0.3]^2[\text{S}^{2-}]}{[0.1]}$$

$$\therefore [\text{S}^{2-}] = \frac{1.3 \times 10^{-20} \times 0.1}{0.09}$$

$$= 1.44 \times 10^{-20} \text{ M}$$

Ex.37 The pH of a 0.01M solution of a monobasic acid is four. Which one of the following statement about the acid is incorrect –

- (A) When a little NaOH is added, it will form a buffer solution
- (B) It is a weak acid
- (C) It's sodium salt will be acidic

(D) It's sodium salt will be basic

Sol. (C)

Concentration of monobasic acid = 0.01 M

$$\text{pH} = 4$$

If the acid is completely ionised the pH of the acid would be

$$\text{pH} = -\log 0.01$$

$$= -\log 10^{-2} = 2$$

So it is a weak acid. The sodium salt of a weak acid when dissolved the anions will be hydrolysed giving rise to OH^- ion concentration. The solution will be basic. So statement (C) is incorrect.

Ex.38 Calculate the amount of $(\text{NH}_4)_2\text{SO}_4$ in gm which must be added to 500 ml of 0.2 M NH_3 to yield a solution of pH = 9, K_b for $\text{NH}_3 = 2 \times 10^{-5}$

(A) 3.248 g (B) 4.248 g

(C) 1.320 g (D) 6.248 g

Sol.

$$(C) \text{ pOH} = -\log K_b + \log \frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]}$$

Let 'a' millimoles of NH_4^+ are added to a solution

having milli moles of $\text{NH}_4\text{OH} = 500 \times 0.2 = 100$

$$\therefore [\text{NH}_4^+] = [\text{salt}] = \frac{a}{500}$$

$$\text{and } [\text{NH}_4\text{OH}] = [\text{Base}] = \frac{100}{500}$$

Given K_b for $\text{NH}_4\text{OH} = 2 \times 10^{-5}$ and pH = 9

$$\therefore 5 = -\log 2 \times 10^{-5} + \log \frac{a/500}{100/500}$$

$$\therefore a = 200 \text{ milli moles} = 0.2 \text{ mol}$$

moles of $(\text{NH}_4)_2\text{SO}_4$ added

$$= \frac{a}{2} = 0.1 \text{ mol}$$

$$\therefore W_{(\text{NH}_4)_2\text{SO}_4} = 0.1 \times 132 = 1.32$$

Ex.39 Calculate the change in pH of 1 litre buffer solution containing 0.1 mole each of NH_3 and NH_4Cl up on addition of ;

(i) 0.02 mole of dissolved gaseous HCl

(ii) 0.02 mole of dissolved NaOH

Assume no change in volume. $K_{\text{NH}_3} = 1.8 \times 10^{-5}$.

Sol. Initial pH of solution when,

$$[\text{NH}_3] = \frac{0.1}{1} \text{ and } [\text{NH}_4\text{Cl}] = \frac{0.1}{1}$$

$$\text{pOH} = -\log 1.8 \times 10^{-5} + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$= -\log 1.8 \times 10^{-5} + \log \frac{0.1}{0.1}$$

$$\text{pOH} = 4.7447$$

$$\therefore \text{pH} = 9.2553$$

(i) Now 0.02 mole of HCl are added, then



Mole before reaction	0.02	0.1	0.1
----------------------	------	-----	-----

Mole after reaction	0	0.08	(0.1 + 0.02)
---------------------	---	------	--------------

\therefore Volume = 1 litre

$$\therefore [\text{NH}_4\text{OH}] = \frac{0.08}{1} \text{ and } [\text{NH}_4\text{Cl}] = \frac{0.12}{1}$$

$$\therefore \text{pOH}_1 = -\log 1.8 \times 10^{-5} + \log \frac{0.12}{0.08}$$

$$\therefore \text{pOH}_1 = 4.9208$$

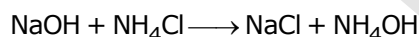
$$\therefore \text{pH}_1 = 9.0792$$

$$\text{Change in pH} = \text{pH} - \text{pH}_1 = 9.2553 - 9.0792$$

$$= +0.1761$$

\therefore Change in pH = 0.1761 and pH decreases

(ii) Now 0.02 mole of NaOH are added



Mole before reaction	0.02	0.1	0.1	0.1
----------------------	------	-----	-----	-----

Mole after reaction	0	0.08	0.02	0.12
---------------------	---	------	------	------

$$\therefore \text{pOH}_2 = -\log 1.8 \times 10^{-5} + \log \frac{0.08}{0.12}$$

$$\text{pOH}_2 = 4.5686$$

$$\therefore \text{pH}_2 = 9.4314$$

$$\text{Change in pH} = \text{pH} - \text{pH}_2 = 9.2553 - 9.4314$$

$$= -0.1761$$

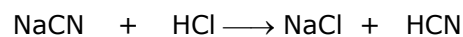
\therefore Change in pH = 0.1761 unit i.e., pH increases

Ex.40 How many mole of HCl will be required to prepare one litre of buffer solution (containing NaCN + HCl) of pH 8.5 using 0.01 g formula weight of NaCN ?

$$K_{\text{HCN}} = 4.1 \times 10^{-10}$$

Sol. NaCN + HCl is not a buffer but if HCl is in less amount then, it gives a buffer as it produces

HCN.



Mole added	0.01	a	0	0
------------	------	---	---	---

Mole after reaction (0.01 - a)	0	a	a	a
--------------------------------	---	---	---	---

This is buffer of HCN + NaCN

Let a mole of HCl be used for this purpose

$$\therefore \text{pH} = -\log K_a + \log \frac{0.01-a}{a}$$

$$8.5 = -\log 4.1 \times 10^{-10} + \log \frac{0.01-a}{a}$$

$$\therefore a = 8.85 \times 10^{-3} \text{ mole of HCl}$$

Ex.41 Calculate the amount of NH_3 and NH_4Cl required to prepare a buffer solution of pH 9.0 when total concentration of buffering reagents is 0.6 mol L^{-1}

Sol. We know,

$$\text{pOH} = -\log K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$5 = 4.7 + \log \frac{a}{b}$$

$$\frac{a}{b} = 2 \quad \therefore a = 2b$$

$$\text{Given } a + b = 0.6$$

$$2b + b = 0.6$$

$$\therefore 3b = 0.6$$

$$\text{or } b = 0.2 \text{ mole or } 0.2 \times 17 = 3.4 \text{ g/L}$$

$$a = 0.4 \text{ mole or } 0.4 \times 53.5 = 21.4 \text{ g/L}$$

$$\text{Thus } [\text{Salt}] = 0.4 \text{ M and } [\text{Base}] = 0.2 \text{ M}$$

Ex.42 A certain buffer solution contains equal concentration of X^- and HX . K_b for X^- is 10^{-10} . Calculate pH of buffer -

Sol. We know,

$$\therefore K_b(\text{X}^-) = 10^{-10}$$

Also for conjugate acid - base pair

$$K_{a_{\text{HX}}} \times K_{b(\text{X}^-)} = 10^{-14}$$

$$K_{a(\text{HX})} \times 10^{-10}$$

$$\text{Now } [\text{HX}] = [\text{X}^-]$$

$$(\text{acid}) \quad (\text{salt})$$

$$\begin{aligned}\therefore \text{pH} &= -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \\ &= -\log 10^{-4} \\ \text{pH} &= 4\end{aligned}$$

Ex.43 Two buffers, (X) and (Y) of pH 4.0 and 6.0 respectively are prepared from acid HA and the salt NaA. Both the buffers are 0.50 M in HA. What would be the pH of the solution obtained by mixing equal volumes of the two buffers? ($K_{\text{HA}} = 1.0 \times 10^{-5}$).

Sol. pH of buffer is given by :

$$\text{pH} = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{For I : } 4 = -\log 1.0 \times 10^{-5} + \log \frac{[\text{Salt}]}{(0.5)}$$

$$\therefore \log \frac{[\text{Salt}]}{0.5} = -1$$

$$\text{or } [\text{Salt}] = 0.1 \times 0.5 = 0.05 \text{ M}$$

$$\text{For II : } 6 = -\log 1.0 \times 10^{-5} + \log \frac{[\text{Salt}]}{0.5}$$

$$\therefore \log \frac{[\text{Salt}]}{0.5} = 1$$

$$\therefore [\text{Salt}] = 10 \times 0.5 = 5 \text{ M}$$

Now the two buffer [(I NaA = 0.05 M and HA = 0.5 M) and (II NaA = 5 M and HA = 0.5 M)] mixed in equal proportion.

Thus, new conc. Of NaA is mixed buffer =

$$\frac{0.05 \times V + 5 \times V}{2V} = \frac{5.05}{2}$$

New con. Of HA in mixed buffer =

$$\frac{0.5 \times V + 0.5 \times V}{2V} = 0.5 \text{ M}$$

$$\text{Thus, pH} = -\log 1.0 \times 10^{-5} + \log \frac{[5.05/2]}{[0.5]}$$

$$\text{pH} = 5 + 0.7033 = 5.7033$$

Ex.44 What amount of sodium propanoate should be added to one litre of an aqueous solution containing 0.02 mole of propanoic acid ($K_a = 1.0 \times 10^{-5}$ at 25°C) to obtain a buffer solution of pH 6 –

- (A) 0.1 M (B) 0.2 M
(C) 0.3 M (D) 1.3 M

Sol. (B)

Using the expression

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{we get, } 6 = -\log(1.0 \times 10^{-5}) + \log \frac{[\text{Salt}]}{[0.02\text{M}]}$$

$$\text{Which gives } 6 = 5 + \log \frac{[\text{Salt}]}{[0.02\text{M}]}$$

$$\text{or } \frac{[\text{Salt}]}{[0.02\text{M}]} = 10 \text{ or } [\text{Salt}] = \mathbf{0.2 \text{ M}}$$

Ex.45 What will be the pH of the solution, if 0.01 mole of HCl is dissolved in a buffer solution containing 0.03 mole of propanoic acid ($K_a = 1.0 \times 10^{-5}$) and 0.02 moles of salt, at 25°C –

- (A) 3.699 (B) 4.699
(C) 5.11 (D) 6.11

Sol. (B)

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= -\log(1.0 \times 10^{-5}) + \log \frac{(0.02 - 0.01)}{(0.03 + 0.01)}$$

$$= 5 + \log \frac{1}{4} = 5 - 0.6$$

$$= \mathbf{4.4}$$

Ex.46 What amount of HCl will be required to prepare one litre of a buffer solution of pH 10.4 using 0.01 mole of NaCN. Given $K_{\text{ion}}(\text{HCN}) = 4.1 \times 10^{-10}$ –

- (A) 8.55×10^{-3} mole (B) 8.65×10^{-3} mole
(C) 8.75×10^{-3} mole (D) 9.09×10^{-4} mole

Sol. (D)

The addition of HCl converts NaCN into HCN. Let x be the amount of HCl added. We will have.

$$[\text{NaCN}] = (0.01 - x)$$

$$[\text{HCN}] = x$$

Substituting these values along with pH and K_a in the expression.

$$\text{pH} = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{We get } 10.4 = -\log[4 \times 10^{-10}] + \log$$

$$\frac{0.01-x}{x} \text{ or } 10.4 = 9.4 + \log \frac{0.01-x}{x}$$

$$\text{or } \log \frac{0.01-x}{x} = 1$$

$$\text{or } \frac{0.01-x}{x} = 10 \Rightarrow 11x = 10^{-2}$$

$$\text{or } x = 9.09 \times 10^{-4} \text{ M}$$

Ex.47 Calculate pH of a solution of given mixture (0.1 mole CH_3COOH + 0.2mole CH_3COONa) in 100 ml of mixture. $K_a = 2 \times 10^{-5}$.

- (A) 5.0 (B) 5.6
(C) 6.6 (D) 7.6

Sol. (A)

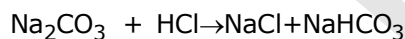
We have

$$\begin{aligned} \text{pH} &= -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \\ &= -\log 2 \times 10^{-5} + \log \frac{\frac{0.2 \times 1000}{100}}{\frac{0.1 \times 1000}{100}} \\ &= 4.7 + 0.3 = 5 \end{aligned}$$

Ex.48 Calculate the pH of a buffer solution prepared by dissolving 10.6gm of Na_2CO_3 in 500 ml of an aqueous solution containing 80 ml of 1M HCl. K_a for $\text{HCO}_3^- = 6 \times 10^{-11}$

- (A) 8.6 (B) 9.6
(C) 11.6 (D) 12.6

Sol. (B)



Meq. before	$\frac{10.6}{106} \times 1000$	80	1	
Reaction	= 100	80	0	0
Meq. After	20	0	80	80
Reaction				

The solution Na_2CO_3 and HCO_3^- and thus acts as buffer

$$\begin{aligned} \text{pH} &= -\log K_a + \log \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \\ &= -\log 6 \times 10^{-11} + \log \frac{20}{80} \\ &= 9.6 \end{aligned}$$

Ex.49 What volume of 0.1 M HCOONa solution should be added to 50ml of 0.05 M formic acid to produce a buffer solution of pH = 4.0, $\text{p}K_a$ of formic acid = 3.7

- (A) 50 ml (B) 40 ml
(C) 30 ml (D) 60 ml

Sol. (A)

Let V ml of 0.1 M HCOONa be mixed to 50ml of 0.05 M HCOOH in mixture

$$[\text{HCOONa}] = \frac{0.1 \times V}{(V+50)}$$

$$[\text{HCOOH}] = \frac{50 \times 0.05}{(V+50)}$$

$$\therefore \text{pH} = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$4.0 = 3.7 + \log \frac{(0.1 \times V)/(V+50)}{2.5/(V+50)}$$

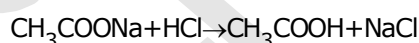
$$V = 50 \text{ ml}$$

Ex.50 Calculate the ratio of pH of a solution containing 1 mole of CH_3COONa + 1mole of HCl per litre and of other solution containing 1 mole CH_3COONa + 1mole of acetic acid per litre.

- (A) 1 : 1 (B) 2 : 1
(C) 1 : 2 (D) 2 : 3

Sol. (C)

Case I - pH when 1mole CH_3COONa and 1 mole HCl are present



Before	1	1	0	0
reaction				
After	0	0	1	1
reaction				

$$[\text{CH}_3\text{COOH}] = 1\text{M}$$

$$\therefore [\text{H}^+] = C\alpha = C \cdot \sqrt{\frac{K_a}{C}} = \sqrt{C \cdot K_a} = \sqrt{K_a}$$

$$\therefore C = 1$$

$$\therefore \text{pH}_1 = -\frac{1}{2} \log K_a$$

Case II - pH when 1 mole CH_3COONa and 1 mole of CH_3COOH , a buffer solution

$$\therefore \text{pH}_2 = -\log K_a + \log T = -\log K_a$$

$$[\text{Salt}] = [\text{Acid}] = 1\text{M}$$

$$\therefore \frac{\text{pH}_1}{\text{pH}_2} = \frac{1}{2} \text{ or } \text{pH}_1 : \text{pH}_2 = 1 : 2$$

Ex.51 Calculate the $\text{pOH} - \text{p}K_b$ for the buffer, 0.20 M NH_3 , 0.40M NH_4Cl , K_b for ammonia = 2×10^{-5}

- (A) 0.50 (B) 0.60
(C) 0.30 (D) 0.75

Sol. (C)

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{Salt}]}{[\text{Base}]};$$

$$\text{pOH} - \text{pK}_b = \log \frac{0.4}{0.2} = 0.30$$

Ex.52 The ionization constant of formic acid is 1.8×10^{-4} . Around what pH will its mixture with sodium formate give buffer solution of higher capacity. Calculate the ratio of sodium formate and formic acid in a buffer of pH 4.25.

Sol. For acidic buffer mixtures.

$$\text{pH} = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{The buffer capacity is } \frac{\text{dpH}}{\text{dn}_{\text{acid or base}}}$$

Thus highest buffer capacity of this is $\frac{\text{dpH}}{\text{dn}_{\text{acid}}}$.

This will be maximum when pH is near to pK_a . Also the best results are obtained by buffer

when $\frac{[\text{Salt}]}{[\text{Acid}]} = 10$ or $\frac{1}{10}$ i.e., within the range

$$\text{pK}_a \pm 1$$

$$\text{Also pH} = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$4.25 = -1.8 \times 10^{-4} + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{or } 4.25 = 3.74 + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\therefore \frac{[\text{Salt}]}{[\text{Acid}]} = 3.24$$

Ex.53 K_{SP} of BaSO_4 is 1.5×10^{-9} . Calculate its solubility in :

(i) pure water; (ii) 0.10 M BaCl_2

Sol. $\text{BaSO}_4 \rightleftharpoons \text{Ba}^{2+} + \text{SO}_4^{2-}$

(i) S S

(where S mole/litre is solubility of BaSO_4)

$$\therefore S = \sqrt{K_{\text{SP}}} = \sqrt{1.5 \times 10^{-9}}$$

$$= 3.87 \times 10^{-5} \text{ mole litre}^{-1}$$

(ii) In presence of 0.10 M BaCl_2 , let S mol/litre BaSO_4 is dissolved

$$K_{\text{SP}} = [\text{Ba}^{2+}] [\text{SO}_4^{2-}]$$

$$1.5 \times 10^{-9} = (0.1 + S) (S)$$

$$[(0.1 + S) = 0.1 \text{ as } \ll 0.1]$$

$$\therefore S = 1.5 \times 10^{-8} \text{ M}$$

Ex.54 $\text{M}(\text{OH})_x$ has $K_{\text{SP}} = 4 \times 10^{-12}$ and its solubility in water is 10^{-4} . Calculate the value of x.

Sol. $\text{M}(\text{OH})_x \rightleftharpoons \text{M}^{x+} + x\text{OH}^-$

$$K_{\text{SP}} = S \cdot (xS)^x \quad \text{Given } S = 10^{-4}$$

$$\text{or } 4 \times 10^{-12} = 10^{-4} \cdot (x \cdot 10^{-4})^x$$

$$10^{-4} \times 10^{-4x} \cdot x^x = 4 \times 10^{-12}$$

$$x^x \cdot (10^{-4})^{1+x} = 4 \times 10^{-12} \quad \therefore x = 2$$

Ex.55 What is the maximum concentration of equimolar solutions of ferrous sulphate and sodium sulphide so that when mixed in equal volumes, there is no precipitation of iron sulphide. For iron sulphide $K_{\text{SP}} = 6.3 \times 10^{-18}$.

Sol. $\text{FeSO}_4 + \text{Na}_2\text{S} \rightarrow \text{FeS} + \text{Na}_2\text{SO}_4$

Let V mL of a molar solution are mixed so that no precipitation of FeS is noticed. Let molarity of FeSO_4 and Na_2S be a M.

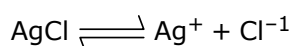
$$\text{Thus, } [\text{Fe}^{2+}] [\text{S}^{2-}] = K_{\text{SP}} = 6.3 \times 10^{-18}$$

$$\left[\frac{a \times V}{2V} \right] \left[\frac{a \times V}{2V} \right] = 6.3 \times 10^{-18};$$

$$\therefore a = 5.02 \times 10^{-9} \text{ M}$$

Ex.56 The solubility product of AgCl in water is 1.5×10^{-10} . Calculate its solubility in 0.01 M NaCl .

Sol. Let solubility be S mol/litre



$$S \quad (S + 0.01)$$

$$K_{\text{SP}} = S \times (S + 0.01)$$

$$= S \times (0.01) \quad (\because S \ll 0.01)$$

$$S = \frac{1.5 \times 10^{-10}}{0.01} = 1.5 \times 10^{-8} \text{ mol/litre.}$$

Ex.57 The solubility of $\text{Pb}(\text{OH})_2$ in water is 6.7×10^{-6} M. Calculate the solubility of $\text{Pb}(\text{OH})_2$ in a buffer solution of $\text{pH} = 8$.

Sol. K_{SP} of $\text{Pb}(\text{OH})_2 = 4s^3 = 4 \times (6.7 \times 10^{-6})^3 = 1.203 \times 10^{-15}$

The buffer contains $\text{pH} = 8 \therefore \text{pOH} = 6$

or $[\text{OH}^-] = 10^{-6}$

Now left solubility of $\text{Pb}(\text{OH})_2$ be s mol litre $^{-1}$ in it

Thus, $[\text{Pb}^{2+}][\text{OH}^-]^2 = K_{\text{SP}}$

$[\text{Pb}^{2+}][10^{-6}]^2 = 1.203 \times 10^{-15}$

[Buffer has $\text{pH} 8, \therefore \text{pOH} = 6$
and $[\text{OH}^-] = 10^{-6}$]

$\therefore [\text{Pb}^{2+}] = \frac{1.203 \times 10^{-15}}{10^{-12}} = 1.203 \times 10^{-3}$ mol litre $^{-1}$

Ex.58 A salt M_2X_3 dissolves in water such that its solubility is x g. mole/litre. Its K_{SP} is –

- (A) x^5 (B) $6x^2$
(C) $108x^5$ (D) $6x^5$

Sol. (C)

Solubility of $\text{M}_2\text{X}_3 = x$ gm mole/litre

$\text{M}_2\text{X}_3 \rightleftharpoons 2\text{M}^{+3} + 3\text{X}^{-2}$

$\therefore [\text{M}^{+3}] = 2x$

$[\text{X}^{-2}] = 3x$

Solubility product $K_{\text{SP}} = (2x)^2 \cdot (3x)^3 = 108x^5$

Ex.59 The solubility of AgCl in water, in 0.02 M CaCl_2 , in 0.01 M NaCl and in 0.05 M AgNO_3 are S_0, S_1, S_2, S_3 respectively. Which of the following relationships between these quantities is correct –

- (A) $S_0 > S_1 > S_2 > S_3$
(B) $S_0 > S_2 > S_1 > S_3$
(C) $S_0 > S_1 = S_2 > S_3$
(D) $S_0 > S_2 > S_3 > S_1$

Sol. (B)

(B) Solubility = $\frac{\text{Solubility Product}}{\text{Concentration of common ion}}$

$$S_1 = \frac{K_{\text{sp}}}{0.02} = 50 K_{\text{SP}}$$

$$S_2 = \frac{K_{\text{sp}}}{0.01} = 100 K_{\text{SP}}$$

$$S_3 = \frac{K_{\text{sp}}}{0.05} = 20 K_{\text{SP}}$$

So, $S_2 > S_1 > S_3$ Again solubility will be greater test in water.

So, $S_0 > S_2 > S_1 > S_3$

Ex.60 Solubility product of AgCl is 2.8×10^{-10} at 25°C . Calculate solubility of the salt in 0.1 M AgNO_3 solution –

- (A) 2.8×10^{-9} mole/litre
(B) 2.8×10^{-10} mole/litre
(C) 3.2×10^{-9} mole/litre
(D) 3.2×10^{-12} mole/litre

Sol. (A)

In 0.1 M AgNO_3

$\text{AgNO}_3 \rightleftharpoons \text{Ag}^+ + \text{NO}_3^-$

$\text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$

$K_{\text{SP}} = [\text{Ag}^+][\text{Cl}^-]$

Now $[\text{Ag}^+]$ can be taken as $[\text{AgNO}_3]$ while $[\text{Cl}^-]$ is the solubility of AgCl

$$\therefore \text{Cl} = \frac{K_{\text{sp}}}{[\text{Ag}^+]} = \frac{2.8 \times 10^{-10}}{0.1}$$

\therefore Solubility of $\text{AgCl} = 2.8 \times 10^{-9}$ mole/litre

Ex.61 K_a for cyanoacetic acid is 4×10^{-3} . What is the value of degree of hydrolysis of 0.4 M sodium cyano acetate solution ?

- (A) 4.5×10^{-6} (B) 5.5×10^{-6}
(C) 2.5×10^{-6} (D) 3.5×10^{-6}

Sol. (C)

$$K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{4 \times 10^{-3}}$$

$$= 0.25 \times 10^{-11}$$

$$h = \sqrt{\frac{K_h}{c}} = \sqrt{\frac{0.25 \times 10^{-11}}{0.4}}$$

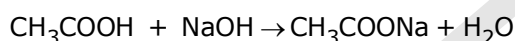
$$= 2.5 \times 10^{-6}$$

Ex.62 Calculate the pH at the equivalence point when a solution of 0.1M acetic acid is titrated with a solution of 0.1M NaOH, K_a for acid = 2×10^{-5} –

- (A) 5.7 (B) 6.7
(C) 7.7 (D) 8.7

Sol. (D)

Let V ml of acid and V ml of NaOH be used
concentration of both acid and NaOH are same.



Concentration before reaction

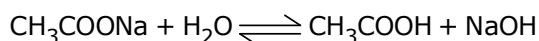
$$\frac{0.1 \times V}{2V} \quad \frac{0.1 \times V}{2V} \quad 0 \quad 0$$

Concentration after reaction

$$0 \quad 0 \quad \frac{0.1 \times V}{2V} \quad \frac{0.1 \times V}{2V}$$

$$[\text{CH}_3\text{COONa}] = \frac{0.1}{2} = 0.05 \text{ M}$$

Now calculate pH by hydrolysis of CH_3COONa



$$[\text{OH}^-] = C \cdot h = \sqrt{\frac{K_w \cdot C}{K_a}}$$

$$= \sqrt{\frac{10^{-14} \times 0.05}{2 \times 10^{-5}}}$$

$$= 5 \times 10^{-6}$$

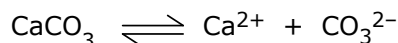
$$p[\text{OH}] = 6 - 0.699 = 5.301$$

$$pH = [14 - 5.301] = \mathbf{8.699 \approx 8.7}$$

Ex.63 The solubility product of chalk is 9.3×10^{-8} .

Calculate its solubility in gram per litre –

- (A) 0.3040 gram / litre
(B) 0.0304 gram / litre
(C) 2.0304 gram / litre
(D) 4.0304 gram / litre

Sol. (B)

Let the solubility of CaCO_3 be s mole per litre

$$\therefore K_{sp} = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] = s \cdot s$$

$$\therefore s = \sqrt{K_{sp}} = \sqrt{9.3 \times 10^{-8}}$$

$$= 0.000304 \text{ mole / litre}$$

Solubility in g/l = mole/litre \times Molecular weight of CaCO_3

$$= 0.000304 \times 100$$

$$= \mathbf{0.0304 \text{ gram / litre}}$$

Ex.64 Calculate the pH of aqueous solution of 1.0 M HCOONH_4 assuming complete dissociation (pK_a of $\text{HCOOH} = 3.8$ and pK_b of $\text{NH}_3 = 4.8$) –

- (A) 3.5 (B) 4.5
(C) 5.5 (D) 6.5

Sol. (D)

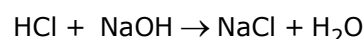
Ammonium formate = salt of (WA + WB)

$$pH = \frac{1}{2} [pK_w + pK_a - pK_b]$$

$$= \frac{1}{2} [14 + 3.8 - 4.8] = \mathbf{6.5}$$

Ex.65 Calculate the pH of a solution which contains 10 ml of 1M HCl and 10 ml of 2 M NaOH

- (A) 11.7 (B) 12.7
(C) 13.7 (D) 10.7

Sol. (C)

Meq. before 10 \times 1 10 \times 2

Reaction = 10 = 20 0 0

Meq. After 0 10 10 10

Reaction

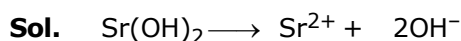
$$[\text{OH}^-] \text{ left from NaOH} = \frac{10}{20} = 0.5 \text{ M}$$

$$\text{pOH} = -\log \text{OH}^- = -\log 0.5$$

$$\text{pOH} = 0.3$$

$$\text{pH} = 13.7$$

Ex.66 The solubility of $\text{Sr}(\text{OH})_2$ at 298 K is 19.23 g/L of solution. Calculate the concentrations of strontium and hydroxyl ions and the pH of the solution.



$$[\text{Sr}(\text{OH})_2] = \frac{19.23}{121.62 \times 1} = 0.158 \text{ M}$$

$$\therefore [\text{OH}^-] = 2 \times 0.158 \text{ M} = 0.316 \text{ M}$$

$$\text{or } \text{pOH} = 0.5003 \quad \therefore \text{pH} = 13.4997$$

$$[\text{Sr}^{2+}] = 0.158 \text{ M}$$

Ex.67 What should be the concentration of NaA. If its 50 mL solution is added to 50 mL of 0.2 M HA to have a pH = 4. K_a for HA = 1.0×10^{-5} .

Sol. Let a be the concentration of NaA.

$$\text{After mixing } M_{\text{NaA}} = \frac{a \times 50}{100} = \frac{a}{2} \text{ and}$$

$$M_{\text{HA}} = \frac{0.2 \times 50}{100} = 0.1$$

$$\text{Now } \text{pH} = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$4 = -\log (1.0 \times 10^{-5}) + \log \frac{a/2}{0.1}$$

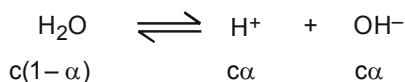
$$\therefore a = 0.2 \text{ M}$$



Solved Example

Ex.1 At 25°C the degree of ionization of water was found to be 1.8×10^{-9} . Calculate the ionization constant and ionic product of water at this temperature

Sol. If α is the degree of ionization of water, then



$$c = [\text{H}_2\text{O}] = \frac{1000}{18} = 55.56 \text{ M}$$

$$K_{\text{eq}} = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \frac{(c\alpha)^2}{c(1-\alpha)} = c\alpha^2 \quad (\text{since } \alpha \text{ is very much less than } 1)$$

than 1)

$$K_{\text{eq}} = 55.56 \times (1.8 \times 10^{-9})^2 = 1.8 \times 10^{-16} \text{ M}$$

$$K_w = [\text{H}^+][\text{OH}^-] = (c\alpha)^2 = (55.56 \times 1.8 \times 10^{-9})^2$$

$$K_w = 1.0 \times 10^{-14} \text{ M}^2$$

Ex.2 (a) Calculate the pH of a 0.01 M solution of benzoic acid, the K_a being 7.3×10^{-5} .

(b) 0.2 M solution of $\text{Ba}(\text{OH})_2$ is found to be 90% ionised at 25°C. Find the pH of the solution at that temperature.

Sol. (a) First calculate α using the expression, $\alpha =$

$$\sqrt{\frac{K_a}{c}} = \sqrt{\frac{7.3 \times 10^{-5}}{0.01}} = 0.085$$

$$\text{pH} = \frac{1}{2}(\text{p}K_a - \log c) = \frac{1}{2}(4.13 - 0.01) = 2.06$$

$$(b) [\text{OH}^-] = 0.2 \times 0.9 \times 2 = 0.36$$

$$\text{pOH} = 0.44; \text{pH} = 13.56$$

Ex.3 What is the pH of a 1.0M solution of acetic acid? To what volume must 1 litre of the solution be diluted so that the pH of the resulting solution will be twice the original value? Given: $K_a = 1.8 \times 10^{-5}$.

Sol. Let us first calculate α using $\alpha = \sqrt{\frac{K_a}{c}}$

$$\alpha = \sqrt{\frac{1.8 \times 10^{-5}}{1}} = 4.24 \times 10^{-3}$$

Since, α is very much smaller than 0.1, so the assumption is valid

$$\therefore [\text{H}^+] = \alpha = 2.19 \times 10^{-5}$$

$$\therefore [\text{H}^+] = \sqrt{K_a \times c} = \sqrt{1.8 \times 10^{-5} \times 1} = 4.24 \times 10^{-3}$$

$$\text{pH} = -\log(4.24 \times 10^{-3}) = 3 - \log 424 = 3 - 0.6273 = 2.37$$

$$\text{Now pH on dilution} = 2 \times 2.37 = 4.74$$

$$[\text{H}^+] = 1.8 \times 10^{-5} = c\alpha$$

$$K_a = \frac{c\alpha^2}{1-\alpha} = \frac{c\alpha \times \alpha}{1-\alpha} = \frac{1.8 \times 10^{-5} \times \alpha}{1-\alpha} = 1.8 \times 10^{-5}$$

$$\frac{\alpha}{1-\alpha} = 1 \quad \therefore \alpha = 0.5$$

$$[\text{H}^+] = ac$$

$$c = \frac{[\text{H}^+]}{\alpha} = \frac{1.8 \times 10^{-5}}{0.5} = 3.6 \times 10^{-5} \text{ M}$$

Let the volume to which 1 l of 1 M acetic acid is diluted be V, then

$$1 \times 1 = 3.6 \times 10^{-5} \times V$$

$$V = \frac{1 \times 1}{3.6 \times 10^{-5}} = \frac{10^5}{3.6} = 0.277 \times 10^4 \text{ litres.}$$

You can notice that α increases on dilution and it becomes considerable and cannot be ignored with respect to 1.

Ex.4 A weak base, BOH is titrated with a strong acid HA. When 10 ml of HA is added, the pH of the solution is 10.2 and when 25 ml is added, the pH of the solution is 9.1. Calculate the volume of acid that would be required to reach equivalence point.

Sol. Let the molarity of HA be ' M_2 ' and the molarity and volume of weak base (BOH) are M_1 and V_1 respectively.

In first case,



$$\begin{array}{ccccccc} \text{mmole before reaction} & M_1V_1 & 10M_2 & 0 & 0 \\ (M_1V_1 - 10M_2) & 0 & 10M_2 & 10M_2 & \end{array}$$

Since the solution (after addition of 10 ml of HA) contains weak base (BOH) and salt of its conjugate base (BA), the solution behaves like a basic buffer.

$$\therefore \text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \quad 14 - 10.2 = \text{p}K_b + \log \frac{10M_2}{(M_1V_1 - 10M_2)}$$

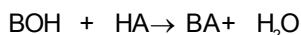
Dividing numerator and denominator of log term by M_2 gives

$$\begin{aligned} 3.8 &= \text{p}K_b + \log \frac{10M_2}{M_2} \\ \therefore 3.8 &= \text{p}K_b + \log \left(\frac{M_1V_1}{M_2} - \frac{10M_2}{M_2} \right) \end{aligned}$$

$$3.8 = \text{p}K_b + \log \frac{10}{V_2 - 10} \quad \dots(i)$$

where V_2 is the volume of acid required to get equivalence point (At equivalence point, $M_1V_1 = M_2V_2$)

In second case,



mmole before reaction M_1V_1 $25M_2$ 0 0

mmole after reaction ($M_1V_1 - 25M_2$) 0 $25M_2$ $25M_2$

$$14 - 9.1 = 4.9 = \text{p}K_b + \log \frac{25M_2}{(M_1V_1 - 25M_2)}$$

Dividing numerator and denominator of log term by M_2

$$4.9 = \text{p}K_b + \log \frac{25}{V_2 - 25} \quad \dots(ii)$$

Subtracting equation (i) from (ii)

$$4.9 - 3.8 = 1.1 = \left(\log \frac{25}{V_2 - 25} \right) - \left(\log \frac{10}{V_2 - 10} \right)$$

$$\text{Taking antilog, } 12.58 = \frac{5V_2 - 50}{2V_2 - 50} \therefore V_2 = 28.72 \text{ ml}$$

Ex.5 20 ml of 0.2 M NaOH is added to 50 ml of 0.2 M acetic acid. What is the pH of the resulting solution? Calculate the additional volume of 0.2 M NaOH required making the solution of pH 4.74. The ionization constant of acetic acid is 1.8×10^{-5} .

Sol. 20 ml of 0.2 M NaOH would react with 20 ml of 0.2 M acetic acid.

$$[\text{Acid}] = 30 \text{ ml of } 0.2 \text{ M present in } 70 \text{ ml} = \frac{30 \times 0.2}{70} = \frac{6}{70} \text{ mole}$$

$$[\text{Salt}] = 20 \text{ ml of } 0.2 \text{ M present in } 70 \text{ ml} = \frac{20 \times 0.2}{70} = \frac{6}{70} \text{ mole}$$

$$\text{p}K_a = -\log 1.8 \times 10^{-5} = 4.74$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{Acid}]} = 4.74 + \log \frac{4}{70} \times \frac{70}{6}$$

$$\text{pH} = 4.74 + \log 0.66 = 4.74 - 0.18 = 4.56$$

To make a solution of pH = 4.74, $[\text{Acid}] = [\text{Salt}]$

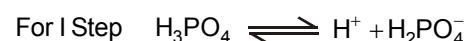
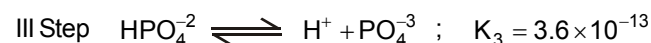
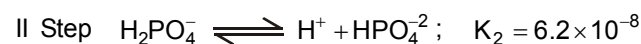
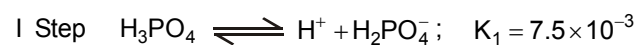
So 25 ml of 0.2 M NaOH must be added to 50 ml of 0.2 M acetic acid.

Addition volume of NaOH to be added = $25 - 20 = 5 \text{ ml}$

Ex.6 Calculate the concentrations of all the species present in 0.1 M H_3PO_4 solution.

Given : $K_1 = 7.5 \times 10^{-3}$, $K_2 = 6.2 \times 10^{-8}$ and $K_3 = 3.6 \times 10^{-13}$.

Sol.



$$\begin{array}{ccc} 0.1 \text{ M} & 0 & 0 \\ (0.1 - c) \text{ M} & c & c \end{array}$$

$$K_1 = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = \frac{c^2}{(0.1 - c)} \quad 7.5 \times 10^{-3} = \frac{c^2}{(0.1 - c)}$$

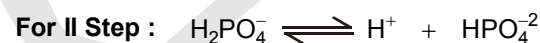
Solving the quadratic equation,

$$c = 0.024$$

$$\therefore [\text{H}^+] = 0.024 \text{ M} \quad \therefore [\text{H}_2\text{PO}_4^-] = 0.024 \text{ M}$$

$$[\text{H}_3\text{PO}_4] = 0.024 \text{ M} \quad [\text{H}_3\text{PO}_4] = 0.1 - 0.024 = 0.076 \text{ M}$$

The value of K_1 is much larger than K_2 and K_3 . Also dissociation of II and III steps occurs in presence of H^+ furnished in I step and thus, dissociation of II and III steps is further suppressed due to common ion effect.



$$\begin{array}{ccc} 0.024 & 0.024 & 0 \\ (0.024 - y) & (0.024 + y) & y \end{array}$$

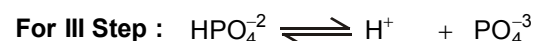
The dissociation of H_2PO_4^- occurs in presence of $[\text{H}^+]$ furnished in step I.

$$\text{Thus, } K_2 = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \text{ or } 6.2 \times 10^{-8} = \frac{(0.024 + y)y}{(0.024 - y)}$$

$$\therefore y \text{ is small } \therefore 0.024 - y \approx 0.024 \text{ and neglecting } y^2.$$

$$\therefore 6.2 \times 10^{-8} = \frac{0.024 y}{0.024} \quad \therefore y = 6.2 \times 10^{-8}$$

$$\text{or } [\text{HPO}_4^{2-}] = K_2 = 6.2 \times 10^{-8} \text{ M}$$



$$(6.2 \times 10^{-8} - x) \quad (0.024 + x) \quad x$$

$$K_3 = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = \frac{(0.024 + x) \cdot x}{(6.2 \times 10^{-8} - x)}$$

Again neglecting x^2 and assuming, $6.2 \times 10^{-8} - x = 6.2 \times 10^{-8}$

$$\therefore 3.6 \times 10^{-13} = \frac{0.024x}{6.2 \times 10^{-8}}$$

$$\therefore [PO_4^{3-}] = x = \frac{3.6 \times 10^{-13} \times 6.2 \times 10^{-8}}{0.024} = 9.3 \times 10^{-19} \text{ M.}$$

Ex.7 The pH of blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentrations. What volume of 5 M $NaHCO_3$ solution, should be mixed with 10 ml sample of blood, which is 2 M in H_2CO_3 in order to maintain a pH of 7.4 K_a for H_2CO_3 in blood is 7.8×10^{-7} ?

Sol. Let the volume of 5 M $NaHCO_3$ solution added be x ml.

Number of millimoles of $NaHCO_3 = 5x$

Number of millimoles of $H_2CO_3 = 10 \times 2 = 20$

For the acidic buffer, $pH = pK_a + \log \frac{[NaHCO_3]}{[H_2CO_3]}$

$$7.4 = -\log(7.8 \times 10^{-7}) + \log \frac{5x}{20}$$

On solving, $x = 78.37$ ml

\therefore Volume of $NaHCO_3$ solution required = 78.37 ml.

Ex.8 An indicator is a weak acid and the pH range of its colour is 3.1 to 4.5. If the neutral point of the indicator lies in the center of the hydrogen ion concentrations corresponding to the given pH range, calculate the ionization constant of the indicator.

Sol. The hydrogen ion concentrations of the given pH range are

For pH 3.1, $pH = -\log [H^+] = 3.1$

$[H^+] = 7.94 \times 10^{-4} \text{ M}$ For pH 4.5,

$pH = 4.5 = -\log [H^+] \therefore [H^+] = 3.16 \times 10^{-5} \text{ M}$

The average of these two hydrogen ion concentrations is

$$\frac{(7.9 \times 10^{-4}) + (3.16 \times 10^{-5})}{2} = 4.128 \times 10^{-4} \text{ M}$$

At this concentration of H^+ , we will get neutral point of the indicator, at which $[In^-] = [HIn]$

$\therefore pH = pK_{HIn}$

or $[H^+] = K_{HIn} = 4.128 \times 10^{-4}$

Ex.9 Calcium lactate is a salt of a weak organic acid and is represented as $Ca(Lac)_2$. A saturated solution of $Ca(Lac)_2$ contains 0.13 mol of this salt in 0.5 litre solution. The pOH of this solution is 5.6. Assuming complete dissociation of the salt, calculate K_a for lactic acid.

Sol. $Ca(Lac)_2(s) \rightarrow Ca(Lac)_2(aq) \rightarrow Ca^{2+}(aq) + 2Lac^-(aq)$



Since it is salt of strong base and weak acid, its pH is calculated as

$$pH = \frac{1}{2}[pK_w + pK_a + \log c] \quad pH = 14 - pOH = 14 - 5.6 = 8.4$$

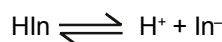
$$8.4 = \frac{1}{2}[14 + pK_a + \log 0.52] \quad (\therefore c = 2 \times 0.13/0.5)$$

$$pK_a = (2 \times 8.4) - 14 - \log 0.52 = 3.08$$

$$\therefore K_a = 8.31 \times 10^{-4}$$

Ex.10 A certain acid - base indicator is red in acid and blue in basic solution. At pH = 5, 75% of the indicator is present in the solution in its blue form. Calculate dissociation constant (K_a) for the indicator and pH range over which the indicator changes from 90% red-10% blue to 90% blue-10% red.

Sol. Since K_a is asked, the indicator must be an acid. Let the acid be represented by HIn .



In acid solution, the indicator will be predominately present in the form of HIn (due to common ion effect.) Since in acid solution the colour is red, this would be due to HIn . In basic solution, the indicator will be predominately in the form of In^- . Since the indicator is blue in basic solution, so In^- must be blue in colour.

At pH = 5, the indicator is 75% blue. This also means it is 25% red.

$$\therefore K_a = \frac{10^{-5} \times 0.75}{0.25} = 3 \times 10^{-5}$$

pH when it is 90% red & 10% blue

$$\therefore [H^+] = \frac{K_a \times [HIn]}{[In^-]} = \frac{3 \times 10^{-5} \times 0.9}{0.1} = 2.7 \times 10^{-4}$$

$$\therefore pH = 3.56$$

pH when it is 90% blue and 10% red :

$$[H^+] = \frac{K_a \times [HIn]}{[In^-]} = \frac{3 \times 10^{-5} \times 0.1}{0.9} = 3.3 \times 10^{-6}$$

Ex.11 Determine the number of mole of AgI which may be dissolved in 1.0 litre of 1.0 M CN⁻ solution.

Given K_{sp} for AgI and K_c for $\text{Ag}(\text{CN})_2^-$ are $1.2 \times 10^{-17} \text{ M}^2$ and $7.1 \times 10^{19} \text{ M}^{-2}$ respectively.

Sol. Given, $\text{AgI(s)} \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{I}^-(\text{aq})$

$$; K_{sp} = [\text{Ag}^+][\text{I}^-] = 1.2 \times 10^{-17} \quad \dots(\text{i})$$



$$; K_f = \frac{[\text{Ag}(\text{CH}_2)]^-}{[\text{Ag}^+][\text{CN}^-]^2} = 7.1 \times 10^{19} \quad \dots(\text{ii})$$

Let 'x' mole of AgI be dissolved in CN⁻ solution, then



Mole before reaction

$$1 \quad 0 \quad 0$$

Mole at equilibrium (1 - 2x) x x

By equations (i) and (ii). $K_{eq} = K_{sp} \times K_f$

$$K_{eq} = \frac{[\text{Ag}(\text{CN})_2]^- [\text{I}^-]}{[\text{CN}^-]^2} = 1.2 \times 10^{-17} \times 7.1 \times 10^{19}$$

$$K_{eq} = 8.52 \times 10^2 \quad \dots(\text{iii})$$

$$\therefore K_{eq} = 8.52 \times 10^2 = \frac{x^2}{(1-2x)^2} \quad \text{or} \quad \frac{x}{1-2x} = 29.2$$

$$\therefore x = 0.49 \text{ mole.}$$

Ex.12 The solubility product of calcium oxalate is 2×10^{-9} at 25°C. Calculate the solubility of calcium oxalate at this temperature. What will be its solubility in a 0.1 M solution of ammonium oxalate? Assume that ammonium oxalate is completely ionized in solution. Name the effect, which operates on addition of ammonium oxalate to calcium oxalate.

Sol. The solubility product, K_{sp} of calcium oxalate is given by

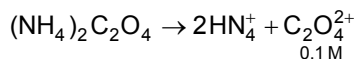
$$K_{sp} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = 2 \times 10^{-9}$$

Let 's' be the solubility of calcium oxalate in mole litre⁻¹.

$$s^2 = 2 \times 10^{-9}$$

$$s = \sqrt{2 \times 10^{-9}} = 4.472 \times 10^{-5} \text{ mole/l.}$$

Let the solubility of CaC_2O_4 be s' in the presence of 0.1 M ammonium oxalate solution.



Since CaC_2O_4 is sparingly soluble, the concentration of $\text{C}_2\text{O}_4^{2-}$ derived from CaC_2O_4 is negligible in comparison to 0.1.

$$K_{sp} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = s' \times 0.1 = 2 \times 10^{-9}$$

$$s' = \frac{2 \times 10^{-9}}{0.1} = 2 \times 10^{-8} \text{ mole/l.}$$

In the presence of ammonium oxalate, the solubility of CaC_2O_4 drops from 4.472×10^{-5} to 2×10^{-8} mole/l. This effect is called common-ion effect.

Ex.13 At 25°C, will a precipitate of $\text{Mg}(\text{OH})_2$ form in a $1 \times 10^{-4} \text{ M}$ solution of $\text{Mg}(\text{NO}_3)_2$ if pH of the solution is adjusted to 9.0. [$K_{sp}(\text{Mg}(\text{OH})_2) = 8.9 \times 10^{-12} \text{ M}^3$]. At which minimum pH will the precipitation start?

Sol. If pH = 9.0, $[\text{H}^+] = 1 \times 10^{-9} \text{ M}$, then

$$[\text{OH}^+] = \frac{K_w}{[\text{H}^+]} = \frac{1 \times 10^{-14}}{1 \times 10^{-9}} = 1 \times 10^{-5} \text{ M}$$

The ionic product of $\text{Mg}(\text{OH})_2$ in the solution would be

$$[\text{Mg}^{2+}][\text{OH}^-]^2 = (1 \times 10^{-4})(1 \times 10^{-5})^2 = 1 \times 10^{-14} \text{ M}^3$$

Since, the value of ionic product is smaller than

$K_{sp}(8.9 \times 10^{-12})$, so no precipitate of $\text{Mg}(\text{OH})_2$ will be formed.

The minimum concentration of OH^- needed to precipitate Mg^{2+} from the solution is

$$[\text{OH}^-] = \sqrt{\frac{K_{sp}}{[\text{Mg}^{2+}]}} = \sqrt{\frac{8.9 \times 10^{-12}}{1 \times 10^{-4}}} = 2.98 \times 10^{-4} \text{ M}$$

$$\therefore \text{Maximum pOH} = 3.54$$

$$\text{and minimum pH} = 14 - 3.54 = 10.46$$

Class Room Problems

Ex.1 Nicotinic acid ($K_a = 1.4 \times 10^{-5}$) is represented by the formula HNic. Calculate its per cent dissociation in a solution which contains 0.10 moles of nicotinic acid per 2.0 litre of solution.

Sol.

Ex.4 A solution contains 0.1 M H_2S and 0.3 M HCl. Calculate the conc. of S^{2-} and HS^- ions in solution. Given K_{a_1} and K_{a_2} for H_2S are 10^{-7} and 1.3×10^{-13} respectively.

Sol.

Ex.2 Calculate the conc. of fluoroacetic acid when $[H^+] = 1.50 \times 10^{-3}$ M. K_a of acid = 2.6×10^{-3} .

Sol.

Ex.5 K_1 and K_2 for dissociation of H_2A is 4×10^{-3} and 1×10^{-5} . Calculate A^{2-} concentration in 0.1 M H_2A solution. Also report $[H^+]$ and pH.

Sol.

Ex.3 A saturated solution of o-nitrophenol, has a pH equal to 4.53. What is the solubility of o-nitrophenol in water pK_a for o-nitro-phenol is 7.23.

Sol.

Ex.6 Calculate the pH of a solution which contains 9.9 mL of 1 M HCl and 100 mL of 0.1 M NaOH.

Sol.

Sol.

Ex.7 What will be the resultant pH when 200 mL of an aqueous solution of HCl (pH = 2.0) is mixed with 300 mL of an aqueous solution of NaOH (pH = 12.0) ?

Sol.

Ex.9 What are $[H^+]$, $[A^-]$ and $[B^-]$ in a solution that is 0.03 M HA and 0.1 M HB ? K_a for HA and HB are 1.38×10^{-4} and 1.05×10^{-10} respectively. Also report pH of solution.

Sol.

Ex.10 Calculate the pH of a solution of given mixtures. (a) (2g CH_3COOH + 3g CH_3COONa) in 100 mL of mixture ; $K_a = 1.8 \times 10^{-5}$. (b) 5 mL of 0.1 M NH_4OH + 250 mL of 0.1 M NH_4Cl ; $K_b = 1.8 \times 10^{-5}$ (c) (0.25 mole of acid + 0.35 mole of salt) in 500 mL mixture; $K_a = 3.6 \times 10^{-4}$.

Sol.

Ex.8 A solution contains 0.09 M HCl, 0.09 M $CHCl_2COOH$ and 0.1 M CH_3COOH . The pH of this solution is 1. If K_a for acetic acid is 10^{-5} , calculate K_a for $CHCl_2COOH$.

Ex.11 20 mL of 0.2 M NaOH is added to 50 mL of 0.2 M acetic acid. ($K_a = 1.8 \times 10^{-5}$) (a) What is pH of solution ? (b) Calculate volume of 0.2 M NaOH required to make the pH of solution 4.74.

Sol.

Ex.12 Two buffers (X) and (Y) of pH 4.0 and 6.0 respectively are prepared from acid HA and the salt NaA. Both the buffers are 0.50 M in HA. What would be the pH of the solution obtained by mixing equal volumes of two buffers ? ($K_{HA} = 1.0 \times 10^{-5}$)

Sol.

Ex.13 A certain buffer solution contains equal concentration of X^- and HX. K_b for X^- is 10^{-10} . Calculate pH of buffer.

Sol.

Ex.14 A weak acid HA after treatment with 12 mL of 0.1 M strong base has a pH of 5. At the end point, the volume of same base required is 26.6 mL. Calculate K_a of acid.

Sol.

Ex.15 The $[Ag^+]$ ion in a saturated solution of Ag_2CrO_4 at $25^\circ C$ is 1.5×10^{-4} M. Determine K_{sp} of Ag_2CrO_4 at $25^\circ C$.

Sol.

Ex.16 Will a precipitate of $\text{Mg}(\text{OH})_2$ be formed in a 0.001 M solution of $\text{Mg}(\text{NO}_3)_2$, if the pH of solution is adjusted to 9? K_{sp} of $\text{Mg}(\text{OH})_2 = 8.9 \times 10^{-12}$.

Sol.

Ex.17 Calculate pH of the following mixture. Given that $K_a = 1.8 \times 10^{-5}$ and $K_b = 1.8 \times 10^{-5}$.

- (a) 50 mL of 0.1 M NaOH + 50 mL of 0.05 M CH_3COOH .
- (b) 50 mL of 0.05 M NaOH + 50 mL of 0.10 M CH_3COOH .
- (c) 50 mL of 0.1 M NaOH + 50 mL of 0.10 M CH_3COOH .
- (d) 50 mL of 0.1 M NH_4OH + 50 mL of 0.05 M HCl.
- (e) 50 mL of 0.05 M NH_4OH + 50 mL of 0.1 M HCl.
- (f) 50 mL of 0.10 M NH_4OH + 50 mL of 0.1 M HCl.
- (g) 50 mL of 0.05 M NH_4OH + 50 mL of 0.05 M CH_3COOH .

Sol.

Ex.18 Assuming no change in volume, calculate the minimum mass of NaCl necessary to dissolve 0.010 mole AgCl in 100 litre solution. K_f for $[\text{AgCl}_2]^- = 3 \times 10^5$ and K_{sp} of AgCl = 1.0×10^{-10} .

Sol.

Ex.19 Calculate the concentration of Fe^{2+} in a solution containing 0.2 M $[\text{Fe}(\text{CN})_6]^{4-}$ and 0.10 M CN^- . K_f for $[\text{Fe}(\text{CN})_6]^{4-} = 1 \times 10^{24}$.

Sol.

EXERCISE – I**OBJECTIVE PROBLEMS (JEE MAIN)**

1. The conjugate acid of NH_2^- is

- (A) NH_3 (B) NH_2OH (C) NH_4^+ (D) N_2H_4

Sol.

2. Out of the following, amphiprotic species are

- I : HPO_3^{2-} II OH^- III H_2PO_4^- IV HCO_3^-

- (A) I, III, IV (B) I and III (C) III and IV (D) All

Sol.

3. pH of an aqueous solution of NaCl at 85°C should be

- (A) 7 (B) > 7 (C) < 7 (D) 0

Sol.

4. 1 c.c. of 0.1N HCl is added to 99 CC solution of NaCl. The pH of the resulting solution will be

- (A) 7 (B) 3 (C) 4 (D) 1

Sol.

5. 10 ml of $\frac{M}{200}\text{H}_2\text{SO}_4$ is mixed with 40 ml of

$\frac{M}{200}\text{H}_2\text{SO}_4$. The pH of the resulting solution is

- (A) 1 (B) 2 (C) 2.3 (D) none of these

Sol.

6. If pK_b for fluoride ion at 25°C is 10.83, the ionisation constant of hydrofluoric acid in water at this temperature is :

- (A) 1.74×10^{-5} (B) 3.52×10^{-3}
(C) 6.75×10^{-4} (D) 5.38×10^{-2}

Sol.

7. The pH of an aqueous solution of 1.0 M solution of a weak monoprotic acid which is 1% ionised is:

- (A) 1 (B) 2 (C) 3 (D) 11

Sol.

8. If K_1 & K_2 be first and second ionisation constant of H_3PO_4 and $K_1 \gg K_2$ which is incorrect.

- (A) $[\text{H}^+] = [\text{H}_2\text{PO}_4^-]$ (B) $[\text{H}^+] = \sqrt{K_1[\text{H}_3\text{PO}_4]}$
(C) $K_2 = [\text{HPO}_4^{2-}]$ (D) $[\text{H}^+] = 3[\text{PO}_4^{3-}]$

Sol.

9. The degree of hydrolysis of a salt of weak acid and weak base in it's 0.1 M solution is found to be 50%. If the molarity of the solution is 0.2 M, the percentage hydrolysis of the salt should be

- (A) 100% (B) 50%
(C) 25% (D) none of these

Sol.

- 10.** What is the percentage hydrolysis of NaCN in $\frac{N}{80}$ solution when the dissociation constant for HCN is 1.3×10^{-9} and $K_w = 1.0 \times 10^{-14}$
- (A) 2.48 (B) 5.26 (C) 8.2 (D) 9.6

Sol.

- 11.** The compound whose 0.1 M solution is basic is
- (A) Ammonium acetate (B) Ammonium chloride
(C) Ammonium sulphate (D) Sodium acetate

Sol.

- 12.** Which of the following solution will have pH close to 1.0 ?

- (A) 100 ml of M/100 HCl + 100 ml of M/10 NaOH
(B) 55 ml of M/10 HCl + 45 ml of M/10 NaOH
(C) 10 ml of M/10 HCl + 90 ml of M/10 NaOH
(D) 75 ml of M/5 HCl + 25 ml of M/5 NaOH

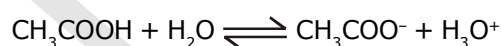
Sol.

- 13.** The \approx pH of the neutralisation point of 0.1 N ammonium hydroxide with 0.1 N HCl is

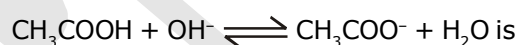
- (A) 1 (B) 6 (C) 7 (D) 9

Sol.

- 14.** If equilibrium constant of



Is 1.8×10^{-5} , equilibrium constant for



- (A) 1.8×10^{-9} (B) 1.8×10^9
(C) 5.55×10^{-9} (D) 5.55×10^{10}

Sol.

- 15.** If 40 ml of 0.2 M KOH is added to 160 ml of 0.1 M HCOOH [$K_a = 2 \times 10^{-4}$]. The pOH of the resulting solution is

- (A) 3.4 (B) 3.7 (C) 7 (D) 10.3

Sol.

16. A solution with pH 2.0 is more acidic than the one with pH 6.0 by a factor of :

- (A) 3 (B) 4
(C) 3000 (D) 10,000

Sol.

17. The first and second dissociation constants of an acid H_2A are 1.0×10^{-5} and 5.0×10^{-10} respectively. The overall dissociation constant of the acid will be:

- (A) 5.0×10^{-5} (B) 5.0×10^{15}
(C) 5.0×10^{-15} (D) 0.2×10^5

Sol.

18. An aqueous solution contains 0.01 M RNH_2 ($K_b = 2 \times 10^{-6}$) & 10^{-4} M NaOH.

The concentration of OH^- is nearly:

- (A) 2.414×10^{-4} M (B) 10^{-4} M
(C) 1.414×10^{-4} M (D) 2×10^{-4} M

Sol.

19. What volume of 0.2 M NH_4Cl solution should be added to 100 ml of 0.1 M NH_4OH solution to produce a buffer solution of pH = 8.7 ?

Given : pK_b of $NH_4OH = 4.7$; $\log 2 = 0.3$

- (A) 50 ml (B) 100 ml
(C) 200 ml (D) none of these

Sol.

Sol.

20. The pK_a of a weak acid, HA, is 4.80. The pK_b of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be:

- (A) 8.58 (B) 4.79
(C) 7.01 (D) 9.22

Sol.

22. How many gm of solid NaOH must be added to 100 ml of a buffer solution which is 0.1 M each w.r.t. Acid HA and salt $Na^+ A^-$ to make the pH of solution 5.5. Given $pK_a(HA) = 5$ (**Use antilog (0.5) = 3.16**)

- (A) 2.08×10^{-1} (B) 3.05×10^{-3}
(C) 2.01×10^{-2} (D) None of these

Sol.

21. The range of most suitable indicator which should be used for titration of $X^- Na^+$ (0.1 M, 10 ml) with 0.1 M HCl should be (Given: $k_{b(X^-)} = 10^{-6}$)

- (A) 2 – 3 (B) 3 – 5 (C) 6 – 8 (D) 8 – 10

23. The solubility of A_2X_3 is y mol dm^{-3} . Its solubility product is

- (A) $6y^2$ (B) $64y^4$ (C) $36y^5$ (D) $108y^5$

Sol.

24. If K_{sp} for $HgSO_4$ is 6.4×10^{-5} , then solubility of this substance in mole per m^3 is

- (A) 8×10^{-3} (B) 6.4×10^{-5}
(C) 8×10^{-6} (D) None of these

Sol.

25. Which of the following is most soluble in water ?

- (A) MnS ($K_{sp} = 8 \times 10^{-37}$)
(B) ZnS ($K_{sp} = 7 \times 10^{-16}$)
(C) Bi_2S_3 ($K_{sp} = 1 \times 10^{-72}$)
(D) $Ag_3(PO_4)$ ($K_{sp} = 1.8 \times 10^{-18}$)

Sol.

26. 1 M NaCl and 1 M HCl are present in an aqueous solution. The solution is

- (A) not a buffer solution and with $pH < 7$
(B) not a buffer solution with $pH > 7$
(C) a buffer solution with $pH < 7$
(D) a buffer solution with $pH > 7$

Sol.

27. the pK_a of a weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA in which 50% of the acid is ionized is:

- (A) 4.5 (B) 2.5 (C) 9.5 (D) 7.0

Sol.

28. The precipitate of CaF_2 ($K_{sp} = 1.7 \times 10^{-10}$) is obtained when equal volumes of the following are mixed

- (A) $10^{-4} M Ca^{3+} + 10^{-4} M F^-$
(B) $10^{-2} M Ca^{2+} + 10^{-3} M F^-$
(C) $10^{-5} M Ca^{2+} + 10^{-3} M F^-$
(D) $10^{-3} M Ca^{2+} + 10^{-5} M F^-$

Sol.

29. pH of saturated solution of silver salt of monobasic acid HA is found to be 9.

Find the K_{sp} of sparingly soluble salt $Ag A(s)$.

Given : $K_a(HA) = 10^{-10}$

- (A) 1.1×10^{-11} (B) 1.1×10^{-10}
(C) 10^{-12} (D) None of these

Sol.

- (A) $10^{-5}M$ (B) $10^{-6}M$
 (C) $10^{-7}M$ (D) None of these

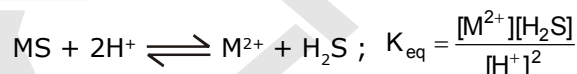
Sol.

30. When equal volumes of the following solutions are mixed, precipitation of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) will occur only with:

- (A) $10^{-4} M$ (Ag^+) and $10^{-4} M$ (Cl^-)
 (B) $10^{-5} M$ (Ag^+) and $10^{-5} M$ (Cl^-)
 (C) $10^{-6} M$ (Ag^+) and $10^{-6} M$ (Cl^-)
 (D) $10^{-10} M$ (Ag^+) and $10^{-10} M$ (Cl^-)

Sol.

32. The solubility of metal sulphides in saturated solution of H_2S ($H_2S = 0.1 M$) can be represented by



The value of K_{eq} is given for few metal sulphide. If conc. of each metal ion in solution is **0.01 M**, which metal sulphides are selectively ppt at total **$[H^+] = 1 M$** in saturated H_2S solution.

Metal sulphides MnS ZnS CoS PbS

$$K_{eq} = \frac{[M^{2+}][H_2S]}{[H^+]^2} \quad 3 \times 10^{10} \quad 3 \times 10^{-2} \quad 3 \quad 3 \times 10^{-7}$$

- (A) MnS, ZnS, CoS (B) PbS, ZnS, CoS
 (C) PbS, ZnS (D) PbS

Sol.

31. 50 litre of a solution containing 10^{-5} mole of Ag^+ is mixed with 50 litre of a $2 \times 10^{-7} M$ HBr solution. $[Ag^+]$ in resultant solution is: [Given : $K_{sp}(AgBr) = 5 \times 10^{-13}$]

33. Solid $Ba(NO_3)_2$ is gradually dissolved in a $1.0 \times 10^{-4} M$ Na_2CO_3 solution. At what concentration of Ba^{2+} will a precipitate begin to form ?
 (K_{sp} for $BaCO_3 = 5.1 \times 10^{-9}$)

- (A) 4.1×10^{-5} M (B) 5.1×10^{-5} M
(C) 8.1×10^{-8} M (D) 8.1×10^{-7} M

Sol.

34. K_{sp} of MX_4 and solubility of MX_4 is S mol/litre is related by:

- (A) $S = [K_{sp}/256]^{1/5}$ (B) $S = [128 K_{sp}]^{1/4}$
(C) $S = [256 K_{sp}]^{1/5}$ (A) $S = [K_{sp}/128]^{1/4}$

Sol.

ASSERTION - REASON

35. Statement-1 : pH of 10^{-7} M NaOH solution is exist between 7 to 7.3 at 25°C .

Statement-2 : Due to common ion effect ionization of water is reduced.

- (A) Statement (1) is correct and statement (2) is correct and statement (2) is correct explanation for (1)
(B) Statement (1) is correct and statement (2) is correct and statement (2) is NOT correct explanation for (1)
(C) Statement (1) is true but (2) is false
(D) Statement (1) is false but (2) is true

Sol.

36. Statement-1 : In general phenolphthalein is used as an indicator for the titration of weak acid (HA) against strong base (NaOH).

Statement-2 : At equivalent point solution is basic.

- (A) Statement (1) is correct and statement (2) is correct and statement (2) is correct explanation for (1)
(B) Statement (1) is correct and statement (2) is correct and statement (2) is NOT correct explanation for (1)
(C) Statement (1) is true but (2) is false
(D) Statement (1) is false but (2) is true

Sol.

37. Statement-1 : Moles of Sr^{2+} of furnished by sparingly soluble substance $\text{Sr}(\text{OH})_2$ decreases due to dilution in its saturated solution.

Statement-2 : Solubility product constant of $\text{Sr}(\text{OH})_2$ is not affected by dilution.

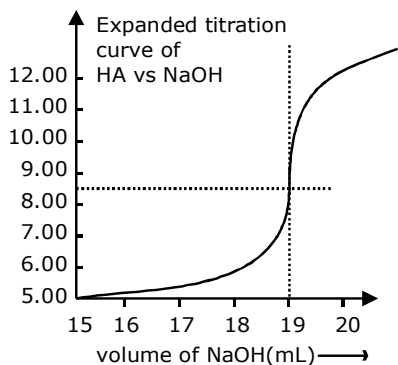
- (A) Statement (1) is correct and statement (2) is correct and statement (2) is correct explanation for (1)
(B) Statement (1) is correct and statement (2) is correct and statement (2) is NOT correct explanation for (1)
(C) Statement (1) is true but (2) is false
(D) Statement (1) is false but (2) is true

Sol.

Comprehension

Paragraph for Question 38 to 40

1.2 of a monoprotic acid HA, is titrated with 0.222 M NaOH solution. The pH of the solution is monitored with pH meter. A portion of the titration curve is shown in the diagram.



38. How many mL of NaOH is required to bring about the titration to its equivalence point?

- (A) 4.00 (B) 9.00
(C) 19.00 (D) None of these

Sol.

39. What is the pH of solution at the equivalence point?

- (A) 3.50 (B) 7.00
(C) 8.40 (D) 5

Sol.

40. What is the molar mass of HA?

- (A) 180 (B) 222
(C) 282 (D) None of these

Sol.

Paragraph for Quesiton 41 to 44

Potash alum is $KAl(SO_4)_2 \cdot 12H_2O$. As a strong eletrolyte, it is considered to be 100% dissociated into K^+ , Al^{3+} and SO_4^{2-} . The solution is acidic because of the hydrolysis of Al^{3+} , but not so acidic as might be expected, because the SO_4^{2-} can sponge up some the H_3O^+ by forming HSO_4^- . Given a solution made by dissolving 11.85 gm of $KAl(SO_4)_2 \cdot 12H_2O$ in enough water to make 100 cm^3 of solution. What is $[H_3O^+]$ of the solution if

41. None of the ion is hydrolysing

- (A) $10^{-7}M$ (B) less than $10^{-7}M$
(C) More than $10^{-7}M$ (D) 0.0

Sol.

42. Only Al^{3+} is hydrolysing and its first hydrolysis constant is 1.4×10^{-5} M

- (A) 1.87×10^{-3} M (B) 6.24×10^{-4} M
(C) 0.09 M (D) None of these

Sol.

43. Only SO_4^{2-} is hydrolysing and acid dissociation constant of HSO_4^- in water is 1.25×10^{-2} .

- (A) 1.26×10^{-3} M (B) 6.32×10^{-7} M
(C) 1.58×10^{-8} M (D) None of these

Sol.

44. Both Al^{3+} and SO_4^{2-} are hydrolysing.

- (A) 2.93×10^{-4} M (B) 0.0114 M
(C) 5.43×10^{-6} M (D) None of these

Sol.

Match The column

45. Column-I

(A) $\left(\begin{array}{l} 10 \text{ litre of } 0.03 \text{ N } \text{X}(\text{OH})_2 \text{ (strong diacidic base)} \\ + \\ 5 \text{ litre of } 0.08 \text{ M } \text{HNO}_3 \\ + \\ 485 \text{ litre of } 0.01 \text{ M } \text{NaNO}_3 \end{array} \right)$

(B) $\left(\begin{array}{l} 10 \text{ ml of } 0.5 \text{ M } \text{RNH}_3\text{Cl} (\text{K}_h = 10^{-9}) \\ + \\ 40 \text{ ml of } 0.125 \text{ M } \text{KOH} \end{array} \right)$

(C) $\left(\begin{array}{l} 100 \text{ ml of } 0.8 \text{ M } \text{HCO}_3^- \\ + \\ 100 \text{ ml of } 0.4 \text{ M } \text{CO}_3^{2-} \\ \left(\text{for } \text{H}_2\text{CO}_3, \text{ use } \text{K}_{a_1} = 4 \times 10^{-7} \text{ \& } \text{K}_{a_2} = 4 \times 10^{-11} \right) \end{array} \right)$

(D) Saturated aqueous solution of $\text{Co}(\text{OH})_3$ ($\text{K}_{sp} = 2.7 \times 10^{-43}$)

Column-II

(P) $\text{pH} \approx 3.7$

(Q) $\text{pH} \approx 11$

(R) $\text{pH} \approx 7$

(S) $\text{pH} \approx 10$

Sol.

46. Column-I (pH of the resultant solution)

(A) 200 ml of H_2SO_4 solution (specific gravity 1.225 containing 25% H_2SO_4 by weight) + 800 ml of 0.525 M strong triacidic base $\text{X}(\text{OH})_3$

(B) 50 ml of 0.1 M HCO_3^- + 50 ml of 0.8 M CO_3^{2-} ($\text{H}_2\text{CO}_3: \text{K}_{a_1} = 4 \times 10^{-7}, \text{K}_{a_2} = 2 \times 10^{-11}$)

(C) 50 ml of 0.2 M $\text{HA}(\text{aq})$ ($\text{K}_a = 10^{-5}$) + 50 ml of 0.1 M $\text{HCl}(\text{aq})$ + 100 ml of 0.13 M $\text{NaOH}(\text{aq})$

Column-II (Exist b/w colour transition range of an indicator)

(P) Phenol Red (6.8 to 8.4)

(Q) Propyl red (4.6 to 6.4)

(R) Phenolphthalein (8.3 to 10.1)

(S) Malachite green (11.4 to 13)

Sol.

Sol.

- 47.** Find the pH of solution prepared by mixing 25ml of a 0.5 M solution of HCl, 10ml of a 0.5 M solution of NaOH and 15ml of water –
- (A) 0.8239 (B) 1.0029
(C) 1.0239 (D) 1.8239

Sol.

- 49.** Determine degree of dissociation of 0.05 M NH_3 at 25°C in a solution of pH = 11.
- (A) 2% (B) 4%
(C) 5% (D) 10%

Sol.

- 50.** Ostwald's dilution law gives satisfactory results for –
- (A) HCl (B) HNO_3
(C) CH_3COOH (D) NaOH

Sol.

- 48.** Which of the following has pH is equal to near about one –
- (A) 100 ml $\frac{M}{10}$ HCl + 100ml $\frac{M}{10}$ NaOH
(B) 55 ml $\frac{M}{10}$ HCl + 44 ml $\frac{M}{10}$ NaOH
(C) 10 ml $\frac{M}{10}$ HCl + 90 ml $\frac{M}{10}$ NaOH
(5) 75 ml $\frac{M}{5}$ HCl + 25ml $\frac{M}{5}$ NaOH

EXERCISE – II**OBJECTIVE PROBLEMS (JEE ADVANCED)**

1. Which of the following statement(s) is/are correct?
 (A) the pH of 1.0×10^{-8} M solution of HCl is 8
 (B) the conjugate base of H_2PO_4^- is HPO_4^{2-}
 (C) autoprotolysis constant of water increases with temperature
 (D) When a solution of a weak monoprotic acid is titrated again a strong base, at half-neutralization point $\text{pH} = (1/2) \text{pK}_a$.

Sol.

2. A 2.5 gm impure sample containing weak monoacidic base (Mol. wt. = 45) is dissolved in 100 ml water and

titrated with 0.5 M HCl when $\left(\frac{1}{5}\right)^{\text{th}}$ of the base was

neutralised the pH was found to be 9 and at equivalent point pH of solution is 4.5. Given : All data at 25°C & $\log 2 = 0.3$.

Select **correct** statement(s).

- (A) K_b of base is less than 10^{-6}
 (B) Concentration of salt (C) at equivalent point is 0.25 M
 (C) Volume of HCl is used at equivalent point is 100 ml
 (D) Weight percentage of base in given sample is 80%

Sol.

3. Select **incorrect** statement(s).

- (A) Phenolphthalein is suitable indicator for the titration of $\text{HCl}(\text{aq})$ with $\text{NH}_4\text{OH}(\text{aq})$.
 (B) An acid-base indicator in a buffer solution of $\text{pH} = \text{pK}_{\text{in}} + 1$ is ionized to the extent of 90%
 (C) In the titration of a monoacidic weak base with a strong acid, the pH at equivalent point is always

calculated by $\text{pH} = \frac{1}{2} [\text{pK}_w - \text{pK}_b - \log C]$

- (D) When $\text{Na}_3\text{PO}_4(\text{aq})$ is titrated with $\text{HCl}(\text{aq.})$, the pH of solution at second equivalent point is calculated

by $\frac{1}{2} [\text{pK}_{a_1} + \text{pK}_{a_2}]$

Sol.

4. Which of the following is true for alkaline aqueous solution?

- (A) $\text{pH} > \frac{\text{pK}_w}{2}$ (B) $\text{pH} > \text{pOH}$ (C) $\text{pOH} < \frac{\text{pK}_w}{2}$ (D) $\text{pH} < \text{pOH}$

Sol.

5. A buffer solution can be prepared from a mixture of

- (A) sodium acetate and acetic acid in water
 (B) sodium acetate and hydrochloric acid in water
 (C) ammonia and ammonium chloride in water
 (D) ammonia and sodium hydroxide in water.

Sol.

6. A solution contains HCl, $\text{Cl}_2\text{HC COOH}$ & CH_3COOH at concentration 0.09 M in HCl, 0.09 M in $\text{Cl}_2\text{HC COOH}$ & 0.1 M in CH_3COOH . pH for the solution is 1. Ionization constant of $\text{CH}_3\text{COOH} = 10^{-5}$. What is the magnitude of K for dichloroacetic acid ?

- (A) $K_a = 1.25 \times 10^{-2}$ (B) $K_a = 2.25 \times 10^{-2}$
 (C) $K_a = 3.75 \times 10^{-4}$ (D) $K_a = 5.75 \times 10^{-2}$

Sol.

7. A solution of chloroacetic acid, ClCH_2COOH containing 9.45 grams in 500 ml of the solution has a pH of 2.0. What is the degree of ionization the acid.

- (A) $\alpha = 0.09$ (B) $\alpha = 0.05$
(C) $\alpha = 0.07$ (D) $\alpha = 0.15$

Sol.

8. The K_w of water at two different temperature is :

T 25°C 50°C

K_w 1.08×10^{-14} 5.474×10^{-14}

Assuming that ΔH of any reaction is independent of temperature, calculate the enthalpy of neutralization of strong acid and strong base.

- (A) $\Delta H_{\text{neut}} = -59.963 \text{ kJ mol}^{-1}$
(B) $\Delta H_{\text{neut}} = -67.967 \text{ kJ mol}^{-1}$
(C) $\Delta H_{\text{neut}} = -62.693 \text{ kJ mol}^{-1}$
(D) $\Delta H_{\text{neut}} = -51.963 \text{ kJ mol}^{-1}$

Sol.

9. The equilibrium constant of the reaction.



is 1.2×10^{-23} at 25°C. Calculate the pH of a solution at equilibrium with the iodine ion concentration = 0.10 and the pressure of H_2 gas = 0.60 atm.

- (A) 3.560 (B) 6.660 (C) 1.650 (D) 5.650

Sol.

10. When a 40 mL of a 0.1 M weak base is titrated with 0.16 M HCl, the pH of the solution at the end point is 5.23. What will be the pH if 15 mL of 0.12 M NaOH is added to the resulting solution.

- (A) 2.861 (B) 9.168 (C) 7.168 (D) 5.816

Sol.

11. How many moles of sodium hydroxide can be added to 1.00 L of a solution 0.1 M in NH_3 & 0.1 M in NH_4Cl without changing the pOH by more than 1.00 unit? Assume no change in volume. $K_b(\text{NH}_3) = 1.8 \times 10^{-5}$.

- (A) 0.0818 moles (B) 0.0516 moles
(C) 0.0718 moles (D) 0.0926 moles

Sol.

12. 20 ml of a solution of 0.1 M CH_3COOH solution is being titrated against 0.1 M NaOH solution. The pH values after the addition of 1 ml & 19 ml of NaOH are $(\text{pH})_1$ & $(\text{pH})_2$, what is ΔpH ?

- (A) 4.858 (B) 8.588
(C) 3.858 (D) 2.558

Sol.

13. Calculate the OH^- concentration and the H_3PO_4 concentration of a solution prepared by dissolving 0.1 mol of Na_3PO_4 in sufficient water to make 1 l of solution. $K_1 = 7.1 \times 10^{-3}$, $K_2 = 6.3 \times 10^{-8}$, $K_3 = 4.5 \times 10^{-13}$.

- (A) $[\text{OH}^-] = 3.73 \times 10^{-18} \text{ M}$, $[\text{H}_3\text{PO}_4] = 6 \times 10^{-3} \text{ M}$
(B) $[\text{OH}^-] = 3.73 \times 10^{-4} \text{ M}$, $[\text{H}_3\text{PO}_4] = 6 \times 10^{-22} \text{ M}$
(C) $[\text{OH}^-] = 3.73 \times 10^{-2} \text{ M}$, $[\text{H}_3\text{PO}_4] = 6 \times 10^{-18} \text{ M}$
(D) $[\text{OH}^-] = 3.73 \times 10^{-4} \text{ M}$, $[\text{H}_3\text{PO}_4] = 6 \times 10^{-16} \text{ M}$

Sol.

14. Solubility product of AgCl is 2.8×10^{-10} at 25°C . Calculate solubility of the salt in 0.1 M AgNO_3 solution-

- (A) 2.8×10^{-9} mole/litre (B) 2.8×10^{-10} mole/litre
(C) 3.2×10^{-9} mole/litre (D) 3.2×10^{-12} mole/litre

Sol.

15. Equilibrium constant for the acid ionization of Fe^{3+} to Fe(OH)^{+2} and H^+ is 6.5×10^{-3} . What is the max. pH, which could be used so that at least 95% of the total Fe^{3+} in a dilute solution, exists as Fe^{3+} .

- (A) 0.608 (B) 2.908 (C) 1.508 (D) 0.908

Sol.

16. A solution of weak acid HA was titrated with base NaOH. The equivalence point was reached when 36.12 ml of 0.1 M NaOH has been added. Now 18.06 ml of 0.1 M HCl were added to titration solution, the pH was found to be 4.92. What will be the pH of the solution obtained by mixing 10 ml 0.2 M NaOH and 10 ml of 0.2 M HA .

- (A) 10.96 (B) 8.96 (C) 12.96 (D) 6.96

Sol.

17. A weak base BOH was titrated against a strong acid. The pH at $1/4$ the equivalence point was 9.24. Enough strong base was now added (6m eq.) to completely convert the salt. The total volume was 50 ml. Find the pH at this point.

- (A) 11.22 (B) 22.44 (C) 33.44 (D) 44.88

Sol.

18. At 25°C , will a precipitate of Mg(OH)_2 form in a 10^{-4} M solution of $\text{Mg(NO}_3)_2$ if pH of the solution is adjusted to 9.0. $K_{sp} [\text{Mg(OH)}_2] = 10^{-11} \text{ M}^3$. At what min value of pH will precipitation start.

- (A) 9 (B) 18 (C) 27 (D) 6

Sol.

19. What is the solubility of AgCl in 0.20 M NH_3 ?

Given : $K_{sp}(\text{AgCl}) = 1.7 \times 10^{-10} \text{ M}^2$, $K_1 = [\text{Ag(NH}_3)^+] / [\text{Ag}^+][\text{NH}_3] = 2.33 \times 10^3 \text{ M}^{-1}$ and

$K_2 = [\text{Ag(NH}_3)_2^+] / [\text{Ag(NH}_3)^+][\text{NH}_3] = 7.14 \times 10^3 \text{ M}^{-1}$

- (A) 6.66×10^{-3} (B) 9.66×10^{-5}
(C) 9.66×10^{-3} (D) 6.66×10^{-5}

Sol.

20. Equal volumes of 0.02 M AgNO_3 and 0.02 M HCN were mixed. Calculate $[\text{Ag}^+]$ at equilibrium. Take $K_a(\text{HCN}) = 9 \times 10^{-10}$, $K_{sp}(\text{AgCN}) = 4 \times 10^{-6}$.

- (A) $[\text{Ag}^+] = 5.699 \times 10^{-5} \text{ M}$ (B) $[\text{Ag}^+] = 6.669 \times 10^{-5} \text{ M}$
(C) $[\text{Ag}^+] = 11.66 \times 10^{-5} \text{ M}$ (D) $[\text{Ag}^+] = 12.669 \times 10^{-5} \text{ M}$

Sol.

EXERCISE – III**SUBJECTIVE PROBLEMS (JEE ADVANCED)**

1. Calculate change in concentration of H^+ ion in one litre of water, when temperature changes from 298 K to 310 K. Given $K_w(298) = 10^{-14}$ $K_w(310) = 2.56 \times 10^{-14}$

Sol.

2. Calculate the number of H^+ present in one ml of solution whose pH is 13.

Sol.

3. pH of dilute solution of HCl is 6.95. Calculate molarity of HCl solution

Sol.

4. Calculate pH of following solutions :

- (a) 0.1 M HCl (b) 0.1 M CH_3COOH ($K_a = 1.8 \times 10^{-5}$)
(c) 0.1 M NH_4OH ($K_a = 1.8 \times 10^{-5}$)
(d) 0.1 M H_2SO_4 (50 ml) + 0.4 M HCl (50 ml)
(e) 10^{-8} M HCl (f) 10^{-10} M NaOH
(g) Decimolar solution of Baryta ($Ba(OH)_2$), diluted 100 times
(h) 10^{-3} mole of KOH dissolved in 100 L of water.
(i) 0.5 M HCl (25 ml) + 0.5 M NaOH (10 ml) + 40 ml H_2O
(j) Equal volume of HCl solution (PH = 4) + 0.0019 N HCl solution
(k) 10^{-6} M CH_3COOH ($K_a = 1.8 \times 10^{-5}$)
(l) 10^{-8} M CH_3COOH ($K_a = 1.8 \times 10^{-5}$)

Sol.

5. Calculate :

- (a) K_a for monobasic acid and whose 0.10 M solution has pH of 4.50
(b) K_b for a monoacidic base whose 0.10 M solution has a pH of 10.50.

Sol.

6. Calculate the ratio of degree of dissociation $\left(\frac{\alpha_2}{\alpha_1}\right)$ when 1 M acetic acid solution is diluted to 1/100 times.
[Given $K_a = 10^{-5} \text{M}$]

Sol.

7. Calculate the ratio of degree of dissociation of acetic acid and hydrocyanic acid (HCN) in 1 M their respective solution of acids.

[Given $K_{a(\text{CH}_3\text{COOH})} = 1.8 \times 10^{-5}$; $K_{a(\text{HCN})} = 6.2 \times 10^{-10}$]

Sol.

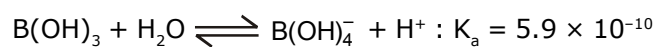
8. The pH of aqueous solution of ammonia is 11.5. Find molarity of solution. $K_b (\text{NH}_4\text{OH}) = 1.8 \times 10^{-5}$.

Sol.

9. The solution of weak monoprotic acid which is 0.01 M has pH = 3. Calculate K_a of weak acid.

Sol.

10. Boric acid is a weak monobasic acid. It ionizes in water as



Calculate pH of 0.3 M boric acid.

Sol.

Sol.

11. Calculate $[H^+]$ and $[CHCl_2COO^-]$ in a solution that is 0.01 M in HCl and 0.01 M in $CHCl_2COOH$.

Take ($K_a = 2.55 \times 10^{-2}$).

Sol.

13. Calculate pH of resultant solution of 0.1 M HA + 0.1 M HB

$[K_a(HA) = 2 \times 10^{-5}; K_a(HB) = 4 \times 10^{-5}]$

Sol.

12. Calculate $[H^+]$, $[CH_3COO^-]$ and $[C_7H_5O_2^-]$ in solution that is 0.02 M in acetic acid and 0.01 M in benzoic acid. K_a (acetic) = 1.8×10^{-5} , K_a (benzoic) = 6.4×10^{-5} .

POLYPROTIC ACIDS & BASES

14. Calculate $[H^+]$, $[H_2PO_4^-]$, $[HPO_4^{2-}]$ and $[PO_4^{3-}]$ in a 0.01 M solution of H_3PO_4 .

Take $K_1 = 10^{-3}$, $K_2 = 10^{-8}$, $K_3 = 10^{-13}$.

Sol.

15. Calculate the pH of 0.1 M solution of $H_2NCH_2CH_2NH_2$; ethylenediamine (en). Determine the en H_2^{2+} concentration in the solution. K_{b1} and K_{b2} values of ethylenediamine are 8.5×10^{-5} and 7.1×10^{-8} respectively.

Sol.

16. What are the concentrations of H^+ , HSO_4^- , SO_4^{2-} and H_2SO_4 in a 0.20 M solution of sulphuric acid?

Given : $H_2SO_4 \rightarrow H^+ + HSO_4^-$; strong

$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$; $K_2 = 10^{-2}$ M

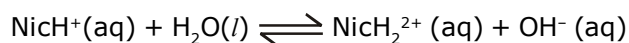
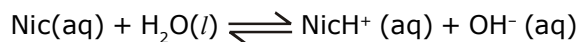
Sol.

17. What are the concentrations of H^+ , $H_2C_2O_4$, $HC_2O_4^-$ and $C_2O_4^{2-}$ in a 0.1 M solution of oxalic acid?

$[K_1 = 10^{-2}$ M and $K_2 = 10^{-5}$ M]

Sol.

18. Nicotine, $C_{10}H_{14}N_2$, has two basic nitrogen atoms and both can react with water to give a basic solution



K_{b1} is 7×10^{-7} and K_{b2} is 10^{-10} . Calculate the approximate pH of 0.020 M solution.

Sol.

19. H_3A is a weak triprotic acid ($K_{a1} = 10^{-5}$, $K_{a2} = 10^{-9}$, $K_{a3} = 10^{-13}$)

Calculate the value of pX of 0.1 M $H_3A(\text{aq})$ solution

where $\text{pX} = -\log X$ & $X = \frac{[A^{3-}]}{[HA^{2-}]}$.

Sol.

BUFFER SOLUTION

20. Determine $[\text{OH}^-]$ of 0.050 M solution of ammonia to which sufficient NH_4Cl has been added to make the total $[\text{NH}_4^+]$ equal to 0.100. [$K_{b(\text{NH}_3)} = 1.8 \times 10^{-5}$]

Sol.

21. Calculate the pH of solution prepared by mixing 50.0 mL of 0.200 M $\text{HC}_2\text{H}_3\text{O}_2$ and 50.0 mL of 0.100 M NaOH. [$K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$]

Sol.

22. A buffer of pH 9.26 is made by dissolving x moles of ammonium sulphate and 0.1 mole of ammonia into 100 mL solution. If pK_b of ammonia is 4.74, calculate value of x .

Sol.

23. 50 mL of 0.1 M NaOH is added to 75 mL of 0.1 M NH_4Cl to make a basic buffer. If pK_a of NH_4^+ is 9.26, calculate pH.

Sol.

24. (a) Determine the pH of a 0.2 M solution of pyridine C_5H_5N . $K_b = 1.5 \times 10^{-9}$

Sol.

(b) Predict the effect of addition of pyridinium ion $C_5H_5NH^+$ on the position of the equilibrium. Will the pH be raised or lowered ?

Sol.

(c) Calculate the pH of 1.0 L of 0.10 M pyridine solution to which 0.3 mol of pyridinium chloride $C_5H_5NH^+Cl$, has been added, assuming no change in volume.

Sol.

25. Calculate the pH of a solution which results from the mixing of 50.0 ml of 0.3 M HCl with 50.0 ml of 0.4 M NH_3 . [$K_b(NH_3) = 1.8 \times 10^{-5}$]

Sol.

26. Calculate the pH of a solution made by mixing 50.0 ml of 0.2 M NH_4Cl & 75.0 ml of 0.1 M NaOH [$K_b(NH_3) = 1.8 \times 10^{-5}$]

Sol.

INDICATORS

27. For the acid indicator thymol blue, pH is 2.0 when half the indicator is in unionised form. Find the % of indicator in unionised form in the solution with $[H^+] = 4 \times 10^{-3}$ M.

Sol.

28. At what pH does an indicator change colour if the indicator is a weak acid with $K_{\text{ind}} = 4 \times 10^{-4}$. For which one(s) of the following neutralizations would the indicator be useful ? Explain.

(a) $\text{NaOH} + \text{CH}_3\text{COOH}$ (b) $\text{HCl} + \text{NH}_3$ (c) $\text{HCl} + \text{NaOH}$

Sol.

Sol.

29. What indicator should be used for the titration of 0.10 M KH_2BO_3 with 0.10 M HCl ?

$$K_a(\text{H}_3\text{BO}_3) = 7.2 \times 10^{-10}$$

Sol.

31. An acid base indicator has a K_a of 3×10^{-5} . The acid form of the indicator is red & the basic form is blue. By how much must the pH change in order to change the indicator from 75% red to 75% blue ?

Sol.

30. Bromophenol blue is an acid indicator with a K_a value of 6×10^{-5} . What % of this indicator is in its basic form at a pH of 5 ?

HYDROLYSIS

32. What is the OH^- concentration of a 0.08 M solution of CH_3COONa . [$K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$]

Sol.

33. Calculate the pH of a 2.0 M solution of NH_4Cl . [$K_b(\text{NH}_3) = 1.8 \times 10^{-5}$]

Sol.

34. 0.25 M solution of pyridinium chloride $\text{C}_5\text{H}_6\text{N}^+ \text{Cl}^-$ was found to have a pH of 2.699. What is K_b for pyridine, $\text{C}_5\text{H}_5\text{N}$?

Sol.

35. Calculate the extent of hydrolysis & the pH of 0.02 M $\text{CH}_3\text{COONH}_4$.

[$K_b(\text{NH}_3) = 1.8 \times 10^{-5}$, $K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$]

Sol.

36. Calculate the percent hydrolysis in a 0.06 M solution of KCN. [$K_a(\text{HCN}) = 6 \times 10^{-10}$]

Sol.

37. Calculate the extent of hydrolysis of 0.005 M K_2CrO_4 . [$K_2 = 3.1 \times 10^{-7}$ for H_2CrO_4]

(It is essentially strong for first ionization)

Sol.

38. Calculate the percent hydrolysis in a 0.0100 M solution of KCN. ($K_a = 6.2 \times 10^{-10}$)

Sol.

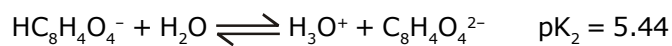
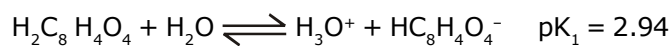
39. A 0.010 M solution of $\text{PuO}_2(\text{NO}_3)_2$ was found to have a pH of 4.0. What is the hydrolysis constant, K_h , for PuO_2^{2+} , and what is K_b for PuO_2OH^+ ?

Sol.

40. Calculate the pH of 1.0×10^{-3} M sodium phenolate, NaOC_6H_5 . for HOC_6H_5 is 1.05×10^{-10}

Sol.

42. Calculate pH of 0.05 M potassium hydrogen phthalate, $\text{KHC}_8\text{H}_4\text{O}_4$.



Sol.

43. The acid ionization (hydrolysis) constant of Zn^{2+} is 1.0×10^{-9}

(a) Calculate the pH of a 0.001 M solution of ZnCl_2

(b) What is the basic dissociation constant of Zn(OH)^+ ?

Sol.

41. What is the pH of 0.1 M NaHCO_3 ? $K_1 = 4.5 \times 10^{-7}$, $K_2 = 4.5 \times 10^{-11}$ for carbonic acids.

Sol.

ACID BASE REACTIONS & TITRATIONS

44. Calculate OH^- concentration at the equivalent point when a solution of 0.1 M acetic acid is titrated with a solution of 0.1 M NaOH. K_a for the acid = 1.9×10^{-5} .

Sol.

45. Calculate the hydronium ion concentration and pH at the equivalence point in the reaction of 22.0 mL of 0.10 M acetic acid, CH_3COOH , with 22.0 mL of 0.10 M NaOH. ($K_a = 1.8 \times 10^{-5}$)

Sol.

46. Calculate the hydronium ion concentration and the pH at the equivalence point in a titration of 50.0 mL of 0.40 M NH_3 with 0.40 M HCl. ($K_b = 1.8 \times 10^{-5}$)

Sol.

47. In the titration of a solution of a weak acid HX with NaOH, the pH is 5.8 after 10.0 mL of NaOH solution has been added and 6.402 after 20.0 mL of NaOH has been added. What is the ionization constant of HX ?

Sol.

48. The equivalent point in a titration of 40.0 mL of a solution of weak monoprotic acid occurs when 35.0 mL of a 0.10 M NaOH solution has been added. The pH of the solution is 5.75 after the addition of 20.0 mL of NaOH solution. What is the dissociation constant of the acid ?

Sol.

49. A weak base (50.0 mL) was titrated with 0.1 M HCl. The pH of the solution after the addition of 10.0 mL and 25.0 mL were found to be 9.84 and 9.24, respectively. Calculate K_b of the base and pH at the equivalence point.

Sol.

50. A weak acid (50.0 mL) was titrated with 0.1 M NaOH. The pH values when 10.0 mL and 25.0 mL of base have been added are found to be 4.16 and 4.76, respectively. Calculate K_a of the acid and pH the equivalence point.

Sol.

51. CH_3COOH (50 ml, 0.1 M) is titrated against 0.1 M NaOH solution. Calculate the pH at the addition of 0 ml, 10 ml, 20 ml, 25 ml, 40 ml, 50 ml of NaOH. K_a of CH_3COOH is 2×10^{-5} .

Sol.

SOLUBILITY & SOLUBILITY PRODUCTS

52. The values of K_{sp} for the slightly soluble salts MX and QX_2 are each equal to 4.0×10^{-18} . Which salt is more soluble ? Explain your answer fully.

Sol.

53. The solubility of $PbSO_4$ in water is 0.038 g/L. Calculate the solubility product constant of $PbSO_4$ in water.

Sol.

54. How many mol CuI ($K_{sp} = 5 \times 10^{-12}$) will dissolve in 1.0 L of 0.10 M NaI solution ?

Sol.

55. A solution of saturated CaF_2 is found to contain 4.1×10^{-4} M fluoride ion. Calculate the K_{sp} of CaF_2 . Neglect hydrolysis.

Sol.

56. The solubility of ML_2 (formula weight, 60 g/mol) in water is 2.4×10^{-5} g/100 mL solution. Calculate solubility product constant for ML_2 .

Sol.

57. What is the solubility (in mol/L) of $Fe(OH)_3$ in a solution of pH = 8.0 ? [K_{sp} for $Fe(OH)_3 = 1.0 \times 10^{-36}$]

Sol.

58. Calculate the solubility of A_2X_3 in pure water, assuming that neither kind of ion reacts with water. For A_2X_3 , $[K_{sp} = 1.1 \times 10^{-23}]$

Sol.

59. Determine the solubility of AgCl in 0.1 M $BaCl_2$. $[K_{sp} \text{ for AgCl} = 1 \times 10^{-10}]$

Sol.

60. What mass of Pb^{2+} ion is left in solution when 50.0 mL of 0.20 M $Pb(NO_3)_2$ is added to 50.0 ml 1.5 M NaCl

[Given K_{sp} for $PbCl_2 = 1.7 \times 10^{-4}$]

Sol.

61. A solution has a Mg^{2+} concentration of 0.0010 mol/L. Will $Mg(OH)_2$ precipitate if the OH^- concentration of the solution is $[K_{sp} = 1.2 \times 10^{-11}]$

(a) 10^{-5} mol/L (b) 10^{-3} mol/L ?

Sol.

62. Calculate solubility of PbI_2 ($K_{sp} = 1.4 \times 10^{-8}$) in water at 25° , which is 90% dissociated

Sol.

63. 500 mL of 0.01 $AgNO_3$ is mixed with 250 ml each of NaBr and NaCl, each having molarity 0.02 M. Find equilibrium concentration of Br^- (moles/L).

Given : $K_{sp}(AgBr) = 5 \times 10^{-13}$, $K_{sp}(AgCl) = 10^{-10}$.

Sol.

64. Calculate solubility of AgCN ($K_{sp} = 4 \times 10^{-16}$) in a buffer solution of PH = 3. [$(K_a)_{HCl} = 4 \times 10^{-10}$]

Sol.

SIMULTANEOUS SOLUBILITY

65. Calculate the Simulataneous solubility of AgSCN and AgBr. $K_{sp}(\text{AgSCN}) = 1.1 \times 10^{-12}$, $K_{sp}(\text{AgBr}) = 5 \times 10^{-13}$.

Sol.

66. Calculate F^- in a solution saturated with respect of both MgF_2 and SrF_2 . $K_{sp}(MgF_2) = 9.5 \times 10^{-9}$, $K_{sp}(SrF_2) = 4 \times 10^{-9}$.

Sol.

COMPLEXATION EQUILIBRIA

67. Assuming no change in volume, calculate the minimum mass of NaCl necessary to dissolve 0.010 mol AgCl in 100 L solution :

[$K_1(\text{AgCl}_2^-) = 3 \times 10^5$, $K_{sp}(\text{AgCl}) = 1 \times 10^{-10}$]

Sol.

68. A recent investigation of the complexation of SCN^- with Fe^{3+} represented by constant K_1 , K_2 and K_3 as 130, 16, and 1.0 respectively. What is the overall formation constant of $Fe(SCN)_3$ from its component ions, and what is the dissociation constant of $Fe(SCN)_3$ into its simplest ions on the basis of these data ?

Sol.

69. How much AgBr could dissolve in 1.0 L of 0.40 M NH_3 ? Assume that $\text{Ag}(\text{NH}_3)_2^+$ is the only complex formed.

$$[K_f(\text{Ag}(\text{NH}_3)_2^+) = 1 \times 10^8 ; K_{sp}(\text{AgBr}) = 5 \times 10^{-13}]$$

Sol.

Sol.

72. A handbook states that the solubility of methylamine $\text{CH}_3\text{NH}_2(\text{g})$ in water at 1 atm pressure at 25°C is 959 volumes of $\text{CH}_3\text{NH}_2(\text{g})$ per volume of water ($\text{p}K_b = 3.39$)

(a) Estimate the max. pH that can be attained by dissolving methylamine in water.

(b) What molarity NaOH (aq.) would be required to yield the same pH ?

Sol.

Miscellaneous

70. Calculate the percent error in the $[\text{H}_3\text{O}^+]$ concentration made by neglecting the ionization of water in 10^{-6} M NaOH solution.

Sol.

73. Mixture of solutions. Calculate the pH of the following solutions. $K_1 = 7.5 \times 10^{-3}\text{ M}$;

$$K_2 = 6.2 \times 10^{-8}\text{ M} ; K_3 = 1.0 \times 10^{-12}\text{ M}$$

(A) 50 ml of $0.12\text{ M H}_3\text{PO}_4$ + 20 ml of 0.15 M NaOH ;

(B) 50 ml of $0.12\text{ M H}_3\text{PO}_4$ + 40 ml of 0.15 M NaOH ;

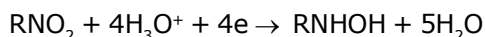
(C) 40 ml of $0.12\text{ M H}_3\text{PO}_4$ + 40 ml of 0.18 M NaOH ;

(D) 40 ml of $0.10\text{ M H}_3\text{PO}_4$ + 40 ml of 0.25 M NaOH .

Sol.

71. What is the pH of 1.0 M solution of acetic acid? To what volume must 1 litre of the solution be dilute so that the pH of the resulting solution will be twice the original value. Given $K_a = 1.8 \times 10^{-5}$.

74. The electrolytic reduction of an organic nitro compound was carried out in a solution buffered by acetic acid and sodium acetate. The reaction was



300 ml of 0.0100 M solution of RNO_2 buffered initially at pH 5.00 was reduced, with the reaction above going to completion. The total acetate concentration, $[\text{HOAc}] + [\text{OAc}^-]$, was 0.50 M. Calculate the pH of the solution after the reduction is complete.

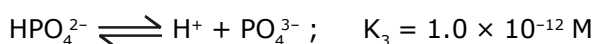
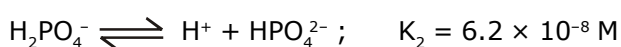
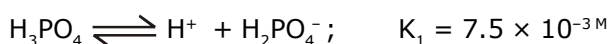
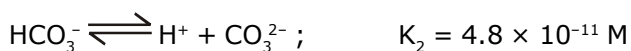
$$(\text{K}_a)_{\text{CH}_3\text{COOH}} = 1.8 \times 10^{-5}$$

Sol.

75. It is desired to prepare 100 ml of a buffer of pH 5.00. Acetic, benzoic and formic acids and their salt are available for use. Which acid should be used for maximum effectiveness against increase in pH? What acid-salt ratio should be used? pK_a values of these acids are : acetic 4.74; benzoic 4.18 and formic 3.68.

Sol.

76. Calculate the pH of 0.1 M solution of (i) NaHCO_3 , (ii) Na_2HPO_4 and (iii) NaH_2PO_4 . Given that ;



Sol.

77. Mixtures of solution. Calculate the pH of the following solution. $\text{K}_1 = 7.5 \times 10^{-3} \text{ M}$;

$$\text{K}_2 = 6.2 \times 10^{-8} \text{ M} ; \quad \text{K}_3 = 1.0 \times 10^{-12} \text{ M}$$

(A) 40 ml of 0.050 M Na_2CO_3 + 50 ml of 0.040 M HCl ;

(B) 40 ml of 0.020 M Na_3PO_4 + 40 ml of 0.040 M HCl ;

(C) 50 ml of 0.10 M Na_3PO_4 + 50 ml of 0.10 M NaH_2PO_4

(D) 40 ml of 0.10 M H_3PO_4 + 40 ml of 0.10 M Na_3PO_4 .

Sol.

78. A buffer solution was prepared by dissolving 0.05 mol formic acid & 0.06 mol sodium formate in enough water to make 1.0 L of solution. K_a for formic acid is 1.80×10^{-4}

(a) Calculate the pH of the solution.

(b) If this solution were diluted to 10 times its volume, what would be the pH?

(c) If the solution in (b) were diluted to 10 times its volume, what would be the pH?

Sol.

79. If 0.0050 mol NaHCO_3 is added to 1 litre of a buffered solution at pH 8.00, how much material will exist in each of the three forms H_2CO_3 , HCO_3^- and CO_3^{2-} ? For H_2CO_3 , $K_1 = 5 \times 10^{-7}$, $K_2 = 5 \times 10^{-13}$.

Sol.

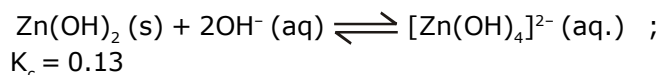
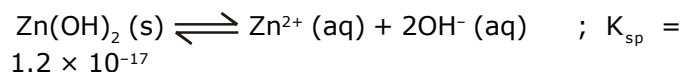
80. The indicator phenol red is half in the ionic form when pH is 7.2. If the ratio of the undissociated form to the ionic form is 1 : 5, find the pH of the solution. With the same pH for solution, if indicator is altered such that the ratio of undissociated form to dissociated form becomes 1 : 4, find the pH when 50% of the new indicator is in ionic form.

Sol.

81. An organic monoprotic acid [0.1M] is titrated against 0.1 M NaOH. By how much does the pH change between one fourth and three fourth stages of neutralization? If at one third stage of neutralization, the pH is 4.45 what is the dissociation constant of the acid? Between what stages of neutralisation may the pH change by 2 units?

Sol.

82. The salt Zn(OH)_2 is involved in the following two equilibria,



Calculate the pH of solution at which solubility is minimum.

Sol.

83. Predict whether or not AgCl will be precipitated from a solution which is 0.02 M in NaCl and 0.05 M in KAg(CN)_2 . Given $K_{\text{inst}}(\text{Ag(CN)}_2^{-}) = 4.0 \times 10^{-19} \text{ M}^2$ and $K_{\text{sp}}(\text{AgCl}) = 2.8 \times 10^{-10} \text{ M}^2$.

Sol.

84. Show that solubility of a sparingly soluble salt $\text{M}^{2+} \text{A}^{2-}$ in which A^{2-} ions undergoes hydrolysis is given by

$$S = \sqrt{K_{\text{sp}} \left(1 + \frac{[\text{H}^+]}{K_2} + \frac{[\text{H}^+]^2}{K_1 K_2} \right)}$$

where K_1 and K_2 are the dissociation constant of acid H_2A . K_{sp} is solubility product of MA.

Sol.

EXERCISE – IV**PREVIOUS YEARS PROBLEMS****LEVEL – I****JEE MAIN**

1. The solubility of $\text{Mg}(\text{OH})_2$ is x mole/ltr. then its solubility product is - **[AIEEE-2002]**

(A) x^3 (B) $5x^3$
(C) $4x^3$ (D) $2x^2$

Sol.

2. The solubility in water of a sparingly soluble salt AB_2 is $1.0 \times 10^{-5} \text{ mol L}^{-1}$. Its solubility product will be - **[AIEEE-2003]**

(A) 1×10^{-15} (B) 1×10^{-10}
(C) 4×10^{-15} (D) 4×10^{-10}

Sol.

3. The molar solubility (in mol L^{-1}) of a sparingly soluble salt MX_4 is 's'. The corresponding solubility product is K_{SP} . 's' is given in terms of K_{SP} by the relation - **[AIEEE-2004]**

(A) $s = (K_{\text{SP}}/128)^{\frac{1}{4}}$ (B) $s = (128K_{\text{SP}})^{\frac{1}{4}}$
(C) $s = (256K_{\text{SP}})^{\frac{1}{5}}$ (D) $s = (K_{\text{SP}}/256)^{\frac{1}{5}}$

Sol.

4. The solubility product of a salt having general formula MX_2 , in water is 4×10^{-12} . The concentration of M^{2+} ions in the aqueous solution of the salt is - **[AIEEE-2005]**

(A) $1.0 \times 10^{-4} \text{ M}$ (B) $2.0 \times 10^{-6} \text{ M}$
(C) $4.0 \times 10^{-10} \text{ M}$ (D) $1.6 \times 10^{-4} \text{ M}$

Sol.

5. The first and second dissociation constants of an acid H_2A are 1.0×10^{-5} & 5.0×10^{-10} respectively. The overall dissociation constant of the acid will be - **[AIEEE-2007]**

(A) 5.0×10^{-5} (B) 5.0×10^{15}
(C) 5.0×10^{-15} (D) 0.2×10^5

Sol.

6. The pK_a of a weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA in which 50% of the acid is ionized is- **[AIEEE-2007]**

(A) 4.5 (B) 2.5
(C) 9.5 (D) 7.0

Sol.

7. In a saturated solution of the sparingly soluble strong electrolyte AgIO_3 (molecular mass = 283) the equilibrium which sets in is -



If the solubility product K_{SP} of AgIO_3 at a given temperature is 1.0×10^{-8} , what is the mass of AgIO_3 contained in 100 ml of its saturated solution? **[AIEEE-2007]**

(A) $28.3 \times 10^{-2} \text{ g}$ (B) $2.83 \times 10^{-3} \text{ g}$
(C) $1.0 \times 10^{-7} \text{ g}$ (D) $1.0 \times 10^{-4} \text{ g}$

Sol.

8. The pK_a of a weak acid, HA, is 4.80. The pK_b of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be - **[AIEEE-2008]**

(A) 4.79 (B) 7.01
(C) 9.22 (D) 9.58

Sol.

9. Solid $\text{Ba}(\text{NO}_3)_2$ is gradually dissolved in a $1.0 \times 10^{-4} \text{ M}$ Na_2CO_3 solution. At what concentration of Ba^{2+} will a precipitate begin to form ?

(K_{sp} for $\text{BaCO}_3 = 5.1 \times 10^{-9}$) [AIEEE-2009]

- (A) $5.1 \times 10^{-5} \text{ M}$ (B) $8.1 \times 10^{-8} \text{ M}$
(C) $8.1 \times 10^{-7} \text{ M}$ (D) $4.1 \times 10^{-5} \text{ M}$

Sol.

10. In aqueous solution the ionization constants for carbonic acid are $K_1 = 4.2 \times 10^{-7}$ and $K_2 = 4.8 \times 10^{-11}$. Selection the correct statement for a saturated 0.034 M solution of the carbonic acid. [AIEEE-2010]

- (A) The concentration of H^+ is double that of CO_3^{2-}
(B) The concentration of CO_3^{2-} is 0.034 M.
(C) The concentration of CO_3^{2-} is greater than that of HCO_3^-
(D) The concentration of H^+ and HCO_3^- are approximately equal.

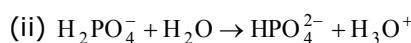
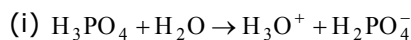
Sol.

11. Solubility product of silver bromide is 5.0×10^{-13} . The quantity of potassium bromide (molar mass taken as 120 g mol^{-1}) to be added to 1 litre of 0.05 M solution of silver nitrate to start the precipitation of AgBr is [AIEEE-2010]

- (A) $5.0 \times 10^{-8} \text{ g}$ (B) $1.2 \times 10^{-10} \text{ g}$
(C) $1.2 \times 10^{-9} \text{ g}$ (D) $6.2 \times 10^{-5} \text{ g}$

Sol.

12. Three reactions involving H_2PO_4^- are given below: [AIEEE-2010]



In which of the above does H_2PO_4^- act as an acid?

- (A) (i) Only (B) (ii) Only
(C) (ii) and (iii) (D) (iii) only

Sol.

13. At 25°C , the solubility product of $\text{Mg}(\text{OH})_2$ is 1.0×10^{-11} . At which pH, will Mg^{2+} ions start precipitating in the form of $\text{Mg}(\text{OH})_2$ from a solution of 0.001 M Mg^{2+} ions ? [AIEEE-2010]

- (A) 8 (B) 9
(C) 10 (D) 11

Sol.

14. The pH of a 0.1 molar solution of the acid HQ is 3. The value of the ionization constant, K_a of this acid is – [AIEEE-2012]

- (A) 1×10^{-3} (B) 1×10^{-5}
(C) 1×10^{-7} (D) 3×10^{-1}

Sol.

15. How many litres of water must be added to litre of an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2? [AIEEE-2013]

- (A) 2.0 L (B) 9.0 L
(C) 0.1 L (D) 0.9 L

Sol.

LEVEL – II

JEE ADVANCED

1. The degree of dissociation of water at 25°C is $2 \times 10^{-7} \%$ and density is 1.0 g cm^{-3} . The ionization constant for water is - **[IIT-1995]**

(A) 1.0×10^{-14} (B) 2.0×10^{-16}
(C) 1.0×10^{-16} (D) 1.0×10^{-8}

Sol.

2. What will be the resultant pH when 200 ml aqueous solution of HCl (pH = 2.0) is mixed with 300 ml of an aqueous solution of NaOH (pH=12.0)? **[JEE 1998]**

Sol.

3. A buffer solution can be prepared from a mixture of - **[IIT-1999]**

(A) Sodium acetate and acetic acid in water
(B) Sodium acetate and hydrochloric acid in water
(C) ammonia and ammonium chloride in water
(D) ammonia and sodium hydroxide in water

Sol.

4. The solubility of $\text{Pb}(\text{OH})_2$ in water is $6.7 \times 10^{-6} \text{ M}$. Calculate the solubility of $\text{Pb}(\text{OH})_2$ in a buffer solution of pH = 8. **[JEE '1999]**

Sol.

5. The pH of 0.1 M solution of the following salts increases in the order **[JEE 1999]**

(A) $\text{NaCl} < \text{NH}_4\text{Cl} < \text{NaCN} < \text{HCl}$
(B) $\text{HCl} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{NaCN}$
(C) $\text{NaCN} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{HCl}$
(D) $\text{HCl} < \text{NaCl} < \text{NaCN} < \text{NH}_4\text{Cl}$

Sol.

6. An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 mL. The volume of 0.1 N NaOH required to completely neutralise 10 mL of this solution is : **[JEE 2001]**

(A) 40 mL (B) 20 mL
(C) 10 mL (D) 4 mL

Sol.

7. For sparingly soluble salt $ApBq$, the relationship of its solubility product (L_s) with its solubility (S) is [JEE 2001]
 (A) $L_s = S^{p+q}$, $p^p \cdot q^q$ (B) $L_s = S^{p+q}$, $p^p \cdot q^p$
 (C) $L_s = S^{p \cdot q}$, $p^p \cdot q^q$ (D) $L_s = S^{p \cdot q}$, $(p \cdot q)^{p+q}$

Sol.

8. 500 ml of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 25°C
 (a) Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.
 (b) If 6 g of NaOH is added to the above solution, determine final pH. Assume there is no change in volume on mixing. K_a of acetic acid is 1.75×10^{-5} M. [JEE 2002]

Sol.

9. A solution which is 10^{-3} M each in Mn^{2+} , Fe^{2+} , Zn^{2+} and Hg^{2+} is treated with 10^{-16} M sulphide ion. If K_{sp} , MnS , FeS , ZnS and HgS are 10^{-15} , 10^{-23} , 10^{-20} and 10^{-54} respectively, which one will precipitate first? [JEE 2003]

- (A) FeS (B) MnS
 (C) HgS (D) ZnS

Sol.

10. Will the pH of water be same at 4°C and 25°C? Explain. [JEE 2003]

Sol.

11. HX is a weak acid ($K_a = 10^{-5}$). It forms a salt NaX (0.1 M) on reacting with caustic soda. The degree of hydrolysis of NaX is [JEE 2004]
 (A) 0.01 % (B) 0.0001%
 (C) 0.1% (D) 0.5%

Sol.

12. 0.1 M of HA is titrated with 0.1 M NaOH, calculate the pH at end point. Given $K_a(\text{HA}) = 5 \times 10^{-6}$ and $\alpha \ll 1$.
[JEE 2003]

Sol.

13. CH_3NH_2 (0.1 mole, $K_b = 5 \times 10^{-4}$) is added to 0.08 moles of HCl and the solution is diluted to one litre, resulting hydrogen ion concentration is
[JEE 2005]

- (A) 1.6×10^{-11} (B) 8×10^{-11}
(C) 5×10^{-5} (D) 2×10^{-2}

Sol.

14. $\text{Ag}^+ + \text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)]^+ ; k_1 = 3.5 \times 10^{-3}$
 $[\text{Ag}(\text{NH}_3)]^+ + \text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+ ;$
 $k_2 = 1.7 \times 10^{-3}$ [JEE 2006]
then the formation constant of $[\text{Ag}(\text{NH}_3)_2]^+$ is
(A) 6.08×10^{-6} (B) 6.08×10^6
(C) 6.08×10^{-9} (D) None of these

Sol.

15. The species present in solution when CO_2 is dissolved in water: [JEE 2006]

- (A) $\text{CO}_2, \text{H}_2\text{CO}_3, \text{HCO}_3^-, \text{CO}_3^{2-}$
(B) $\text{H}_2\text{CO}_3, \text{CO}_3^{2-}$
(C) $\text{CO}_3^{2-}, \text{HCO}_3^-$
(D) $\text{CO}_2, \text{H}_2\text{CO}_3$

Sol.

16. Solubility product constant (K_{sp}) of salts of types MX, MX_2 and M_3X at temperature 'T' are 4.0×10^{-8} , 3.2×10^{-14} and 2.7×10^{-15} , respectively. Solubilities (mol. dm^{-3}) of the salts at temperature 'T' are in the order [JEE 2008]

- (A) $\text{MX} > \text{MX}_2 > \text{M}_3\text{X}$ (B) $\text{M}_3\text{X} > \text{MX}_2 > \text{MX}$
(C) $\text{MX}_2 > \text{M}_3\text{X} > \text{MX}$ (D) $\text{MX} > \text{M}_3\text{X} > \text{MX}_2$

Sol.

17. 2.5 mL of $\frac{2}{5}$ M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°C) is titrated with $\frac{2}{15}$ M HCl in water at 25°C . The concentration of H^+ at equivalence point is ($K_w = 1 \times 10^{-14}$ at 25°C)
[JEE 2008]

- (A) 3.7×10^{-13} M (B) 3.2×10^{-7} M
(C) 3.2×10^{-2} M (D) 2.7×10^{-2} M

Sol.

18. The dissociation constant of a substituted benzoic acid at 25°C is 1.0×10^{-4} . The pH of a 0.01 M solution of its sodium salt is :

[JEE 2009]

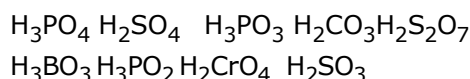
Sol.

19. Aqueous solutions of HNO_3 , KOH , CH_3COOH , and CH_3COONa of identical concentrations are provided. The pair(s) of solutions which form a buffer upon mixing is(are). [JEE 2010]

- (A) HNO_3 and CH_3COOH
 (B) KOH and CH_3COONa
 (C) HNO_3 and CH_3COONa
 (D) CH_3COOH and CH_3COONa

Sol.

20. The total number of diprotic acids among the following is [IIT-2010]



Sol.

21. In 1 L saturated solution AgCl [$K_{\text{sp}}(\text{AgCl}) = 1.6 \times 10^{-10}$], 0.1 mol of CuCl [$K_{\text{sp}}(\text{CuCl}) = 1.0 \times 10^{-6}$] is added. The resultant concentration of Ag^+ in the solution is 1.6×10^{-x} . The value of "x" is [JEE 2011]

Sol.

22. The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12} at 298 K. The solubility (in mol/L) of Ag_2CrO_4 in a 0.1 M AgNO_3 solution is [IIT-2013]

- (A) 1.1×10^{-11} (B) 1.1×10^{-10}
 (C) 1.1×10^{-12} (D) 1.1×10^{-9}

Sol.

23. The initial rate of hydrolysis of methyl acetate (1M) by a weak acid (HA , 1M) is $1/100^{\text{th}}$ of a strong acid (HX , 1M) at 25°C. The K_a of HA is [IIT-2013]

- (A) 1×10^{-4} (B) 1×10^{-5}
 (C) 1×10^{-6} (D) 1×10^{-3}

24. The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12} at 298 K. The solubility (in mol/L) of Ag_2CrO_4 in a 0.1 M AgNO_3 solution is

- (A) 1.1×10^{-11} (B) 1.1×10^{-10}
 (C) 1.1×10^{-12} (D) 1.1×10^{-9}

Answers

Answer Ex-I

OBJECTIVE PROBLEMS (JEE MAIN)

- | | | | | | | | |
|-------|-------|-------|-------|------------------------|-------------------|-------|-------|
| 1. A | 2. C | 3. C | 4. B | 5. B | 6. C | 7. B | 8. D |
| 9. B | 10. A | 11. D | 12. D | 13. B | 14. B | 15. D | 16. D |
| 17. C | 18. D | 19. C | 20. C | 21. B | 22. A | 23. D | 24. D |
| 25. D | 26. A | 27. C | 28. B | 29. A | 30. A | 31. C | 32. D |
| 33. B | 34. A | 35. A | 36. B | 37. D | 38. C | 39. C | 40. C |
| 41. A | 42. A | 43. C | 44. A | 45. A-P, B-Q, C-S, D-R | 46. A-S, B-S, C-Q | | |
| 47. A | 48. D | 49. A | 50. C | | | | |

Answer Ex-II

OBJECTIVE PROBLEMS (JEE ADVANCED)

- | | | | | | | | |
|--------|--------|----------|----------|----------|-------|-------|-------|
| 1. B,C | 2. B,C | 3. A,B,C | 4. A,B,C | 5. A,B,C | 6. A | 7. B | 8. D |
| 9. C | 10. B | 11. A | 12. D | 13. C | 14. A | 15. D | 16. B |
| 17. A | 18. A | 19. C | 20. B | | | | |

Answer Ex-III

SUBJECTIVE PROBLEMS (JEE ADVANCED)

- | | | |
|--|------------------------|--------------------------|
| 1. 0.6×10^{-7} | 2. 6.022×10^7 | 3. 2.31×10^{-8} |
| 4. (a) 1 (b) 2.87 (c) 11.13 (d) 0.522 (e) 6.97 (f) 7 (g) 11.30 (h) 9 (i) 1 (j) 3 (k) 6.01 (l) 6.97 | | |
| 5. (a) $K_a = 10^{-8}$ (b) $K_b = 10^{-6}$ | | |

6. 10 7. 170.4 8. 0.556 9. 1.11×10^{-4} 10. 4.87
11. $[H^+] = 1.612 \times 10^{-2} M$, $[CHCl_2COO^-] = 6.126 \times 10^{-3} M$ 12. $[H^+] = 10^{-3} M$, $[CH_3COO^-] = 3.6 \times 10^{-4} M$, $[C_7H_5O_2^-] = 6.4 \times 10^{-4} M$
13. 2.61 14. $[H^+] = [H_2PO_4^-] = 2.7 \times 10^{-3}$, $[HPO_4^{2-}] = 10^{-8}$, $[PO_4^{3-}] = 3.7 \times 10^{-19}$ 15. $pH = 11.46$, $[enH_2^{2+}] = 7.1 \times 10^{-8}$
16. 0.2116 M, 0.1884 M, 0.0116 M, 0 17. 0.027M, 0.073 M, 0.027M, $10^{-5} M$ 18. 10.07
19. 10 20. 9.0×10^{-6} 21. 4.74 22. 0.05 mol 23. 9.56
24. (a) $pH = 9.239$ (b) Lowered (c) $pH = 4.699$ 25. 8.7782 26. 9.7324
27. $[HIn] = 28.57 \%$ 28. (b) & (c) 29. Methyl red, one with $pH = 5.22$ as mid point of colour change
30. 85.71 % 31. $\Delta pH = 0.954$ 32. $[OH^-] = 6.664 \times 10^{-6}$ 33. $pH = 4.477$
34. $K_b = 6.25 \times 10^{-10}$ 35. 0.56%, $pH = 7$ 36. 1.667% 37. 0.26% 38. 4%
39. 10^{-6} , 10^{-8} 40. $pH = 10.43$ 41. 8.34 42. 4.19 43. (a) 6 (b) 1×10^{-5} 44. $5.12 \times 10^{-6} M$
45. 8.71 46. 4.98 47. $pK_a = 6.1$ 48. 2.37×10^{-6} 49. $K_b = 1.8 \times 10^{-5}$, 5.27 50. 8.73
51. (i) 2.85 (ii) 4.0969 (iii) 4.5229 (iv) 4.699 (v) 5.301 (vi) 8.699 52. QX_2 is more soluble 53. 1.6×10^{-8}
54. $[Cu^+] = 5 \times 10^{-11} M$ 55. 3.4×10^{-11} 56. 2.6×10^{-16} 57. $1 \times 10^{-18} M$
58. $1 \times 10^{-5} \text{ mol/L}$ 59. $5 \times 10^{-10} M$ 60. 12 mg
61. (a) no ppt will occur (b) a ppt will form 62. 1.6×10^{-3} 63. 2.49×10^{-5}
64. 2.1×10^{-5} 65. $9 \times 10^{-7} M$, $4 \times 10^{-7} M$ 66. $[F^-] = 3 \times 10^{-3} M$ 67. 19.5 kg

68. $K_d = \frac{1}{K_f} = 4.8 \times 10^{-4}$ 69. $2.8 \times 10^{-3} \text{ M}$ 70. error = 1% 71. $V = 2.77 \times 10^4 \text{ litre}$
72. (a) 13.1 (b) 0.13 M 73. (a) 2.12 (b) 4.66 (c) 7.2 (d) 12 74. 5.158
75. acetic acid, salt-acid molar ratio 1.8 : 1 76. 8.35, 9.60, 4.66 77. (a) 8.34 (b) 4.66 (c) 9.6 (d) 7.20
78. (a) pH = 3.83 (b) pH = 3.85, (c) = 3.99 79. $[\text{H}_2\text{CO}_3] = 9.85 \times 10^{-6} \text{ M}$; $[\text{HCO}_3^-] = 4.9 \times 10^{-4}$ $[\text{CO}_3^{2-}] = 2.45 \times 10^{-8}$
80. pH = 7.3 81. 0.9542 82. 9.99, $s = 10^{-9} \text{ M}$ 83. ppt. will occur

Answer Ex-IV**PREVIOUS YEARS PROBLEMS****LEVEL – I****JEE MAIN**

1. C 2. C 3. D 4. A 5. C 6. C 7. B
8. B 9. A 10. D 11. C 12. B 13. C 14. B
15. B

LEVEL – II**JEE ADVANCED**

1. B 2. pH=11.3010 3. AC 4. $s = 1.203 \times 10^{-3} \text{ M}$ 5. B
6. A 7. A 8. (a) 0.0175% (b) 4.757 9. C
10. No it will be > 7 11. A 12. pH = 9 13. B
14. A 15. A 16. D 17. D 18. pH = 8 19. C,D
20. 6 21. 7 22. B 23. A 24. B